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RAY T. BAYLESS, *Editor*

Vol. XXIX **December 1941** **No. 4**

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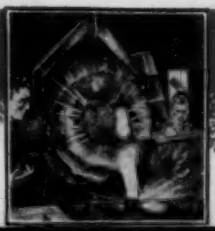

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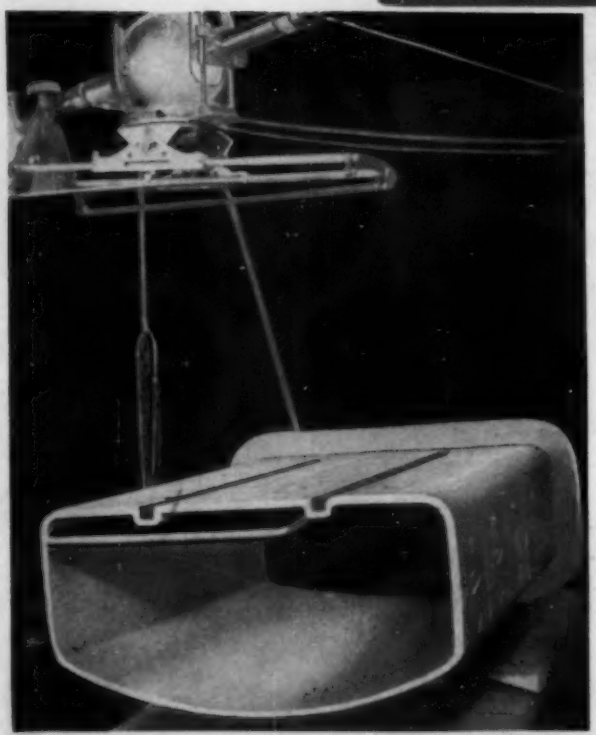

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THE STRUCTURE AND RATE OF FORMATION OF PEARLITE

By Robert F. Mehl

Abstract

This lecture is an account of a study of the austenite: pearlite transformation in simple-carbon eutectoid steels in terms of the rate of formation of nuclei and the rate of growth of these nuclei. The austenitizing reaction is considered from this point of view; the structure and the mode of formation of pearlite are described, and the results of the application of the electron microscope to the study of the structure of steel announced; and data are given on the rate of nucleation and rate of growth of pearlite correlated with austenitizing treatment and the degrees of austenite heterogeneity which this determines.

THOSE who have thought about the matter seem generally in agreement that the professor's chief duty, apart from his primary duty of the training of students, is to add to what is known concerning the basic principles of his subject—those fundamental principles that underlie the more immediate practical engineering applications. Thinking on this, it seemed to me that when a professor is called upon to deliver the Campbell Lecture, he could not do better than to try to interest his audience in an account of the development of the basic science in some part of the field of metallurgy, provided that his subject pertains to at least one of the practical interests of his hearers. And it seemed not inappropriate to select the subject of pearlite, for pearlite is of general metallurgical interest and some new facts about it have been unearthed in recent years.

It was not long after 1886 when Sorby (1)[1] first viewed pearl-

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

This is the Sixteenth Edward DeMille Campbell Memorial Lecture, October 22, 1941, presented by Robert F. Mehl, Director, Metals Research Laboratory, and Head, Department of Metallurgical Engineering, Carnegie Institute of Technology, Pittsburgh. The lecture was presented at the Twenty-third Annual Convention of the Society, held in Philadelphia, October 20 to 24, 1941.

This lecture is printed herewith substantially as delivered. The new experimental work reported will subsequently be published in detail.

ite under the microscope, Fig. 1, that Osmond (2), following the work of Tschernoff (3), determined the critical points in steel as a function of the carbon content and as a function of the rate of heating and cooling, and it was very shortly thereafter that metallurgists observed that the critical temperature A_1 is associated with the formation of pearlite.

It had been stated by Arnold and McWilliam (4) and by Benedicks (5) as early as the year 1905 that pearlite forms by a process

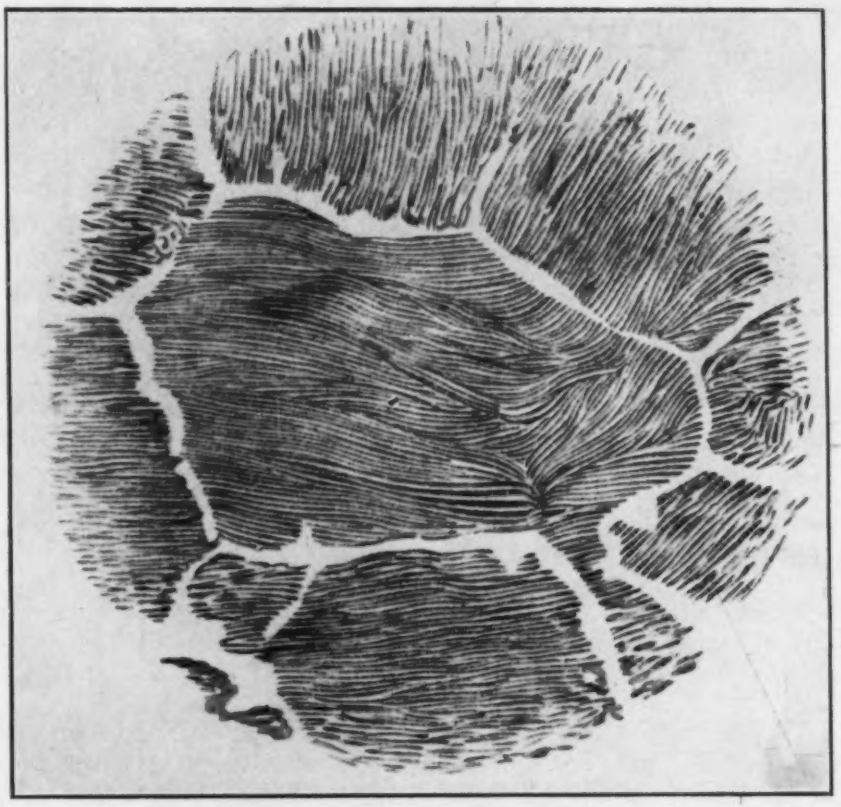

Fig. 1—Sketch of Pearlite by Sorby. (1886).

of nucleation and growth. Howe and Levy in 1916 (6) speculated upon how the rapid formation of pearlite at low temperatures may at least in part be determined by an increase in the rate of nucleation. The work of Davenport and Bain in 1930 (7) on the isothermal reaction curve and the derived S-curve served to emphasize with great clarity the fact that the formation of pearlite is a process of nucleation and growth of pearlite nodules, and served to establish the basic fact that the critical cooling rate for hardening in simple carbon eutectoid steels is determined by the maximum rate at which this

process of nucleation and growth proceeds—the rate of formation of pearlite at the knee of the S-curve.

Accepting the fact that pearlite forms by a process of nucleation and growth, it should be possible to obtain a deeper insight into the operation of the variables affecting the rate of formation of pearlite by studying them in terms of a rate of formation of pearlite nuclei and a rate of growth of these nuclei. Such a study would analyze the isothermal reaction curve into the two factors which determine it, that is, the rate of nucleation and the rate of growth, and such a method of study would therefore be one step beyond that of the isothermal reaction curve and the S-curve.

My own interest in matters of this sort originated years ago when Professor Donald Smith of Princeton first introduced me to the fundamental work of the great Tammann on nucleation and growth processes (8). What I shall have to say now will be chiefly an account of that which we have learned during the last few years at the Carnegie Institute of Technology concerning the structure of pearlite and concerning the formation of pearlite from this point of view. I well realize the risks that attend the presentation of new data—it would, of course, be safer to present old information newly disguised, but I should think it would be less interesting.

With the great importance of pearlite to the metallurgical industry, experimental studies of this sort seem justified. That great prophet of our scientific age, Francis Bacon, expressed the hope that knowledge will be progressive. He hoped that upon one fact, one discovery, another will be built, and upon that another, and upon that still again another, each perfecting the last, so that the structure of knowledge will continue to grow and grow. The man and the scholar whom we honor today, Edward DeMille Campbell, was one of the modern generation of scientists, a man whose aim was to help to build our knowledge of metals. He was interested in the structure and the constitution of steel, he brought new methods to its study, and he added new and important chapters to our knowledge of it; he was indeed a true disciple of Francis Bacon. How well he succeeded as a teacher and as a research worker is shown by his successful students, his many publications, and by the honor that has been shown him in the establishment of the Campbell Memorial Lecture.

What I shall say here that is new, is the result of the labors of

this subject: Messrs. W. A. Johnson, F. C. Hull, G. V. Smith, G. E. Pellissier, Jr., M. F. Hawkes, G. A. Roberts, and R. A. Colton. I know that Professor Campbell would have understood the satisfaction I have had in associating with this group of very able students.

The Characteristics of Nucleation and Growth Processes

Let us, then, first discuss nucleation and growth processes in a general way, hoping that a general discussion will enlighten the subsequent discussion of real cases. It should be said immediately that

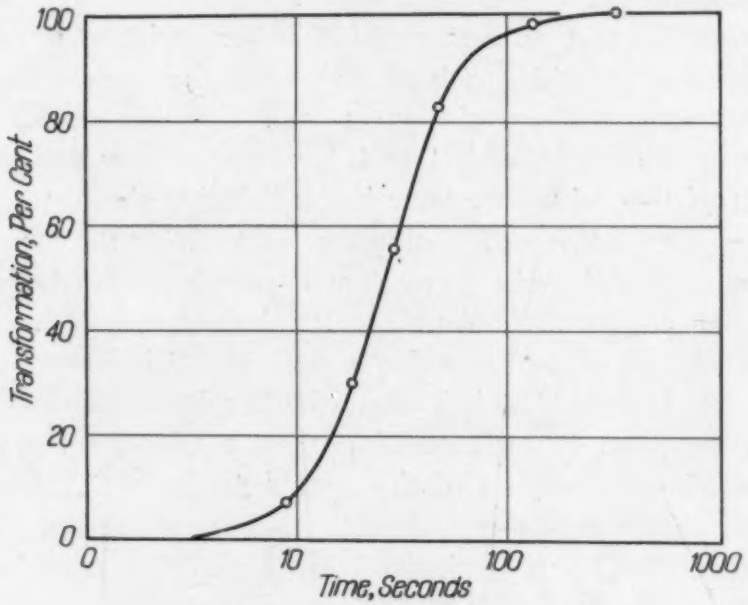

Fig. 2—A Typical Isothermal Reaction Curve.

the characteristics of nucleation and growth processes are of wide fundamental importance, applying not only to reactions of the sort we are considering, but also to many other reactions of metallurgical importance, among which are freezing, recrystallization, and precipitation from solid solution (9). And let us approach this subject by a consideration of the isothermal reaction curve.

The isothermal reaction curve is determined by a rate of nucleation and a rate of growth (9). It has the shape typified by that shown in Fig. 2. This curve represents the percentage of transformation product formed during isothermal reaction as a function of time. At first the rate of the reaction is slow, then it accelerates, reaching a maximum at about fifty per cent transformation, and then

decelerates. The initial period seems long, and it has been suggested that this is an incubation period during which the matrix is preparing itself to react, but this is an unnecessary conception, for the form of the curve in the initial period is the expected one on the basis that nuclei form with time at a constant rate, and grow with time at a constant rate, as shown by v. Göler and Sachs some years ago (10).

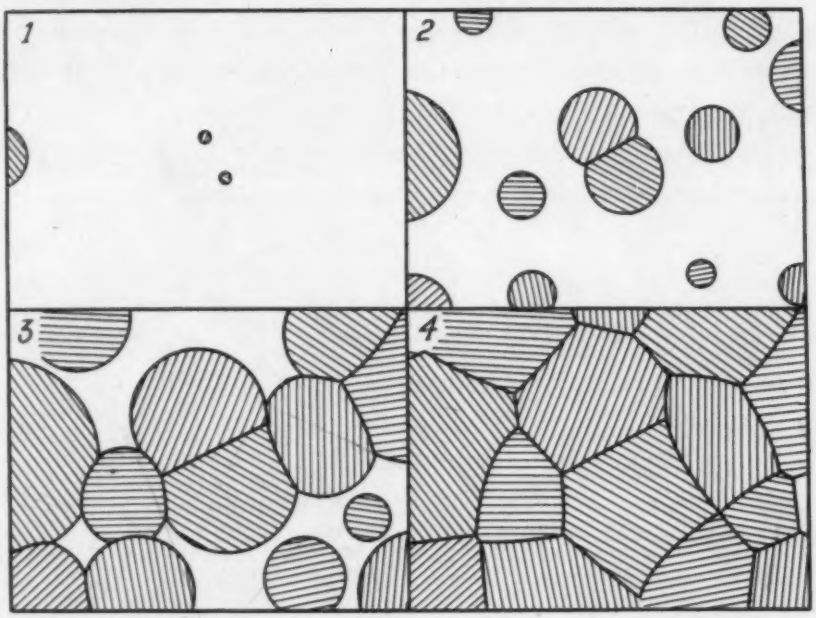

Fig. 3—Diagram Depicting the Progress of a Nucleation and Growth Process. Four Stages at Equal Time Intervals.

The process of reaction by a nucleation and growth process may be readily pictured, Fig. 3. The transformation starts by the formation of nuclei, and during the reaction these nuclei continue to form, and of course to grow. These nuclei are pictured as forming at random in the untransformed matrix; the number which forms per second in a given volume of untransformed matrix is the rate of nucleation. Each nucleus after birth begins to grow; the rate at which its radius increases with time is the rate of growth.

The isothermal reaction is pictured in Fig. 3 in four stages at equal time intervals. As the reaction proceeds with nuclei forming steadily and each steadily growing, the nodules inevitably impinge upon one another. Such impingement is shown in the second stage and has become extensive in the third stage. The impingement exerts a retarding effect upon the rate of reaction, and this retardation

becomes effective enough to decrease the overall rate of reaction in the neighborhood of fifty per cent transformation, and from there steadily to decrease it.

Accordingly, the isothermal reaction curve is a result of the combined effects of a certain rate of nucleation and a certain rate of growth. The curve can be calculated from assumed or measured values of these quantities, and the calculated curve is found to reproduce the experimental curve accurately, as Johnson has shown for the formation of pearlite from austenite (9). It is an easy matter to predict how alterations in the two component rates will affect the curve, increasing the overall rate or decreasing it. And in summary it may therefore be said that there is no uncertainty whatsoever concerning the mechanism of such reactions.

The Rate of Isothermal Austenitizing

It is to be understood, then, that pearlite forms from austenite by a process consisting in the nucleation and the growth of pearlite nodules. It is our main purpose to consider this process, but in order to do so with clarity we need first to make inquiry into the degrees of homogeneity that can be attained in austenite, for these degrees of homogeneity exercise an effect upon the rate of formation of pearlite.

The formation of austenite from pearlite likewise proceeds by a process of nucleation and growth, as emphasized by Grossmann in recent years (12). It should, therefore, provide isothermal reaction curves similar to those for the formation of pearlite as first obtained by Bain, and Roberts has shown recently it does (11).

Fig. 4 presents a series of photomicrographs displaying the process of the austenitizing reaction operated isothermally, in which the progressive nucleation and growth of austenite nodules in a matrix of pearlite are clearly evident. The similarity between these photomicrographs and the diagram presented earlier is obvious.

The rate of austenitizing shown by these photomicrographs can be conveniently represented by an isothermal austenitizing rate curve, Fig. 5. It must be stated immediately and quite clearly that these curves do not represent the formation of homogeneous austenite: they represent merely the disappearance of lamellar pearlite. At the termination of the curves at one hundred per cent reaction, globules of carbide remain; at longer times these disappear, and their dis-

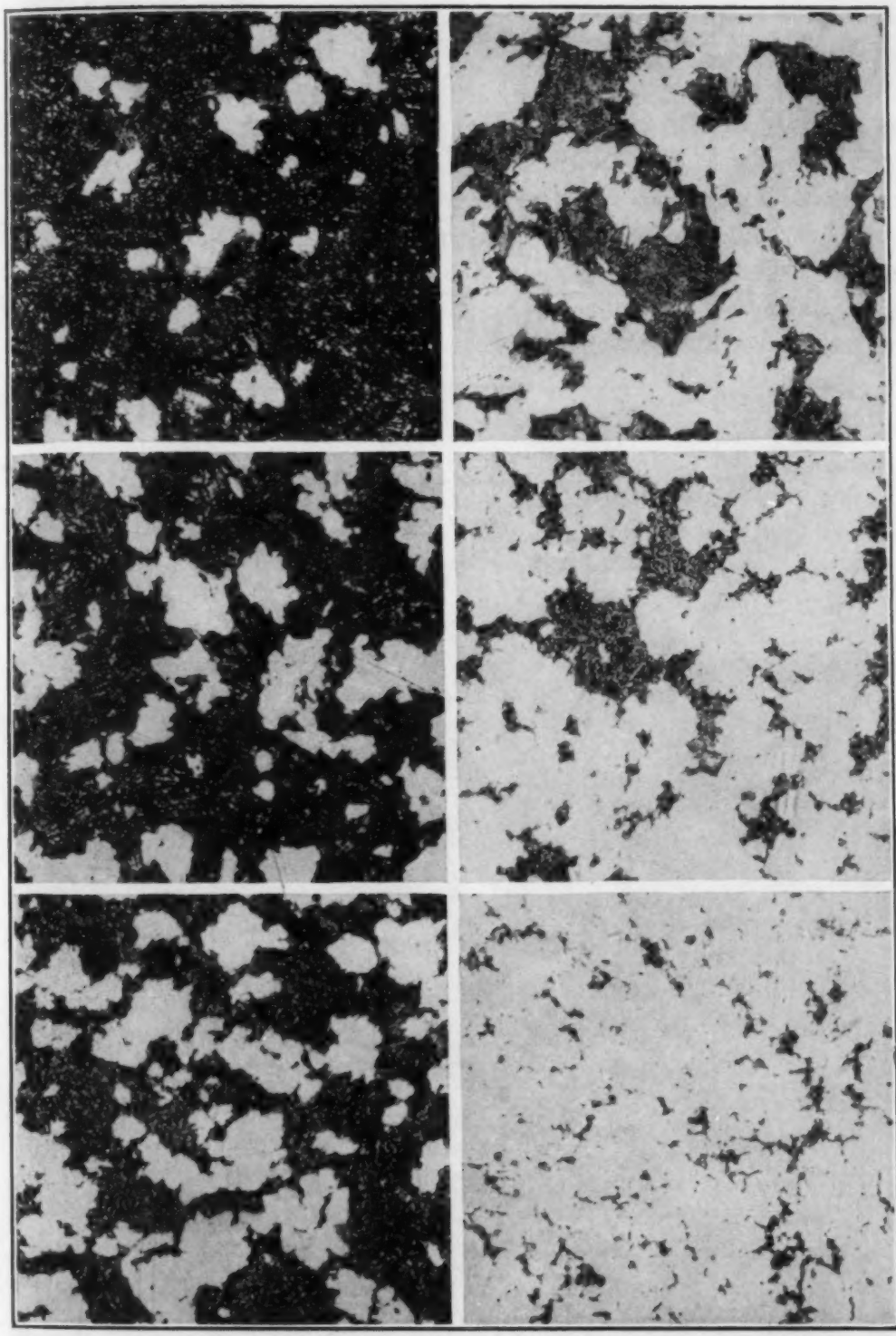

Fig. 4—Progressive Austenitizing. Showing Nucleation and Growth of Austenite Nodules. Eutectoid Steel. Austenitized at 1355 Degrees Fahr. (735 Degrees Cent.) for 10, 20, 30, 35, 40 and 55 Seconds. Etchant—Nital. × 250.

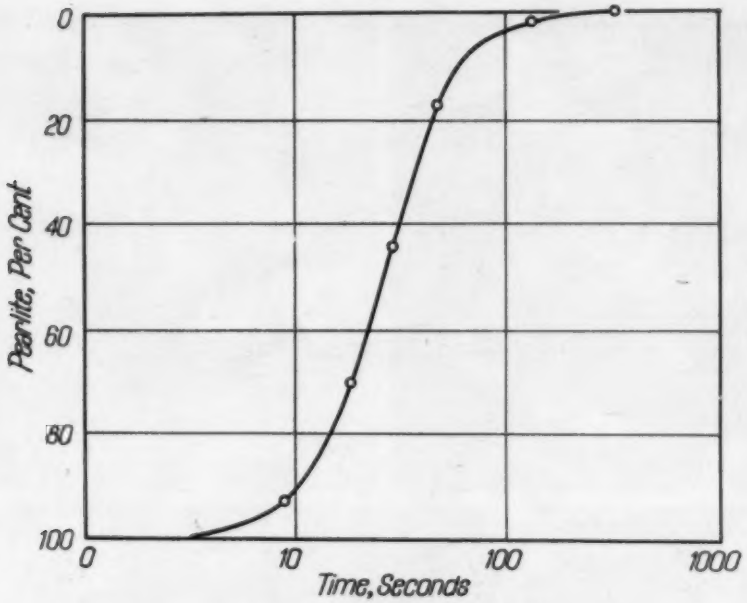

Fig. 5—A Typical Isothermal Austenitizing Curve.

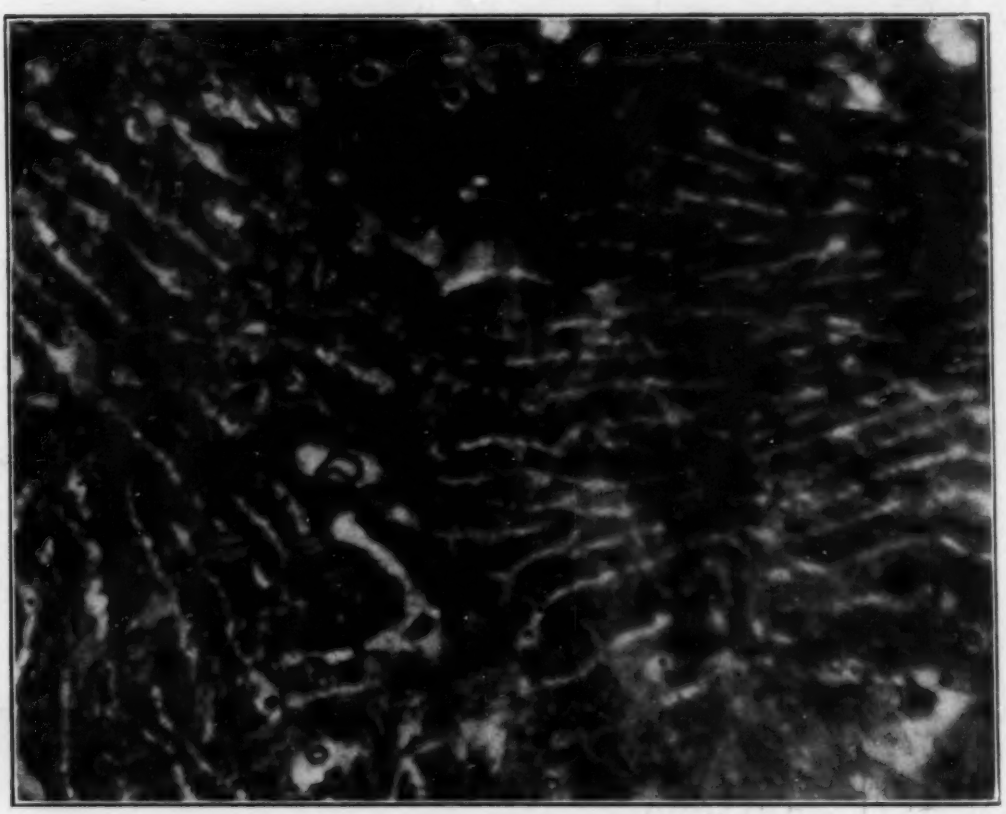

Fig. 6—Pearlite "Ghosts". Eutectoid Steel, Austenitized at 1475 Degrees Fahr. (800 Degrees Cent.) for 10 Minutes, Water Quenched. Etched with Double Strength Sodium Picrate. × 2500.

appearance may be followed microscopically, but even then carbon concentration gradients remain. Some years ago Hultgren (13) demonstrated in a paper before this society that such gradients can be revealed by a special etching technique, Fig. 6, which develops "pearlite ghosts," showing where the pearlitic carbide had just disappeared by solution, leaving lamellae of *austenite* of high carbon concentration, accurately delineating the original pearlite. These undissipated gradients are dissipated in time, though at the moment we have no satisfactory method of determining the time course of this homogenization process.

The Austenitizing S-Curve

Now it will be remembered that isothermal reaction curves at different temperatures for the decomposition of austenite are usually assembled into an "S-curve," which then pictures the rate of reaction over the whole temperature interval (*7*). It should be, and it is possible also to assemble isothermal austenitizing reaction curves into an isothermal austenitizing rate-temperature curve, Fig. 7, showing "beginning" and "end" curves for the disappearance of pearlite, a curve for the final solution of carbide, and a curve for the ultimate dissipation of carbon concentration gradients, though the last curve is necessarily schematic for these gradients cannot disappear at a sharp point in time (11). It will be noted that the disappearance of pearlite is extremely rapid; at 1384 degrees Fahr. (750 degrees Cent.) fine pearlite in a previously normalized eutectoid steel, was observed to disappear in 25 seconds, and the reaction was too rapid to be observed at 70 degrees Fahr. above Ae_1; but the solution of residual carbides is comparatively a much slower process, as the figure shows, owing presumably to the lower active carbon concentration gradients.

Variables Affecting the Rate of Isothermal Austenitizing

The isothermal austenitizing curves can be accurately reproduced by inserting the proper values of the rate of nucleation and the rate of growth into the proper analytical expression, as may be seen in Fig. 8, which shows also the measured rate of nucleation and rate of growth (11). The interaction of the rate of nucleation and the rate of growth determines the resultant austenitic grain size,

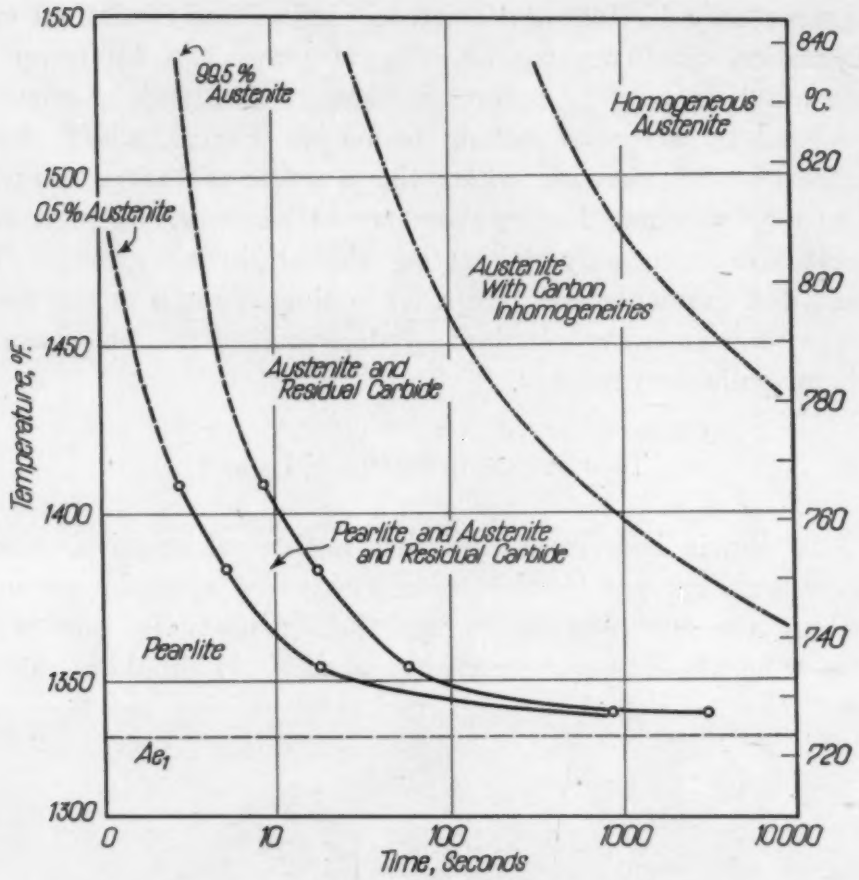

Fig. 7—Austenitizing Rate-Temperature Curves for Commercial Simple-Carbon Eutectoid Steel. Prior Treatment—Normalized from 1610 Degrees Fahr. (875 Degrees Cent.). Initial Structure—Fine Pearlite. First Curve at Left Shows Beginning Disappearance of Pearlite. Second Curve Shows Final Disappearance of Pearlite. Third Curve Shows Final Disappearance of Carbide. Fourth Curve Shows Final Disappearance of Carbon Concentration Gradients.

and it appears that the factors determining austenite grain size might profitably be inspected from this point of view.

The important variables which determine the rate of austenitizing are different from those which determine the rate of formation of pearlite. Upon austenitizing, two variables appear important: first, the chemical composition of the steel, and second, the interlamellar spacing in pearlitic steels, or the degree of coarseness of the carbide dispersion in spheroidized steels. In the seventh Campbell Lecture in 1932, Bain (14) stated that fine pearlite austenitizes much more rapidly than coarse spheroidized carbide; in 1939 Lauderdale and Harder (15) studied the rate of solution of gross carbides in detail, as had Digges and Jordan in 1935 (16). As we

shall see later, many workers have recognized the influence of undissolved carbide and heterogeneous austenite upon hardenability, though there is little quantitative information.

The importance of the interlamellar spacing on the rate of austenitizing has been demonstrated by Roberts (11); Fig. 9 gives isothermal austenitizing curves for the fine- and coarse-grained steels,

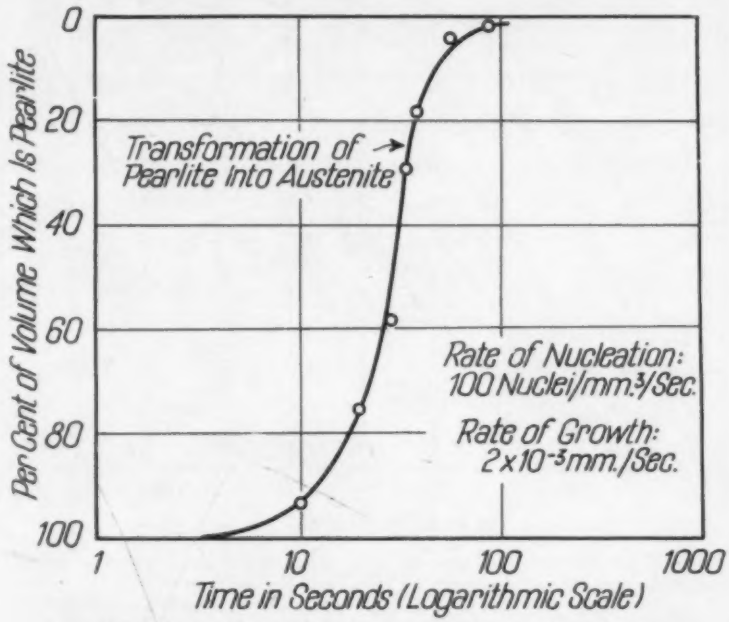

Fig. 8—An Isothermal Austenitizing Curve. Points are Experimental Values. Full Curve is Curve Calculated From Rate of Nucleation and Rate of Growth Noted on Figure.

prepared from the same heat of steel by Cash, Merrill, and Stephenson and reported upon by them at the meeting of this Society October, 1940 (17). A sample of each was isothermally reacted to pearlite at each of three sub-critical temperatures, thus providing three pairs of samples of equal pearlite spacing; the samples with equal spacing are those reacted to pearlite at the same temperature, as shown in the figure—those reacted at the lower temperature naturally have the smaller interlamellar spacing. It is clear from the figure, that the rate of austenitizing is the greater the finer the spacing for either of the steels, as would be expected. The reasons for this are simple: the dissolution of pearlite to austenite is obviously a process dependent upon diffusion, and since the distance through which carbon must diffuse is the greater for the coarser pearlite, the rate of growth of the austenite nodule should be the lower, as it is observed to be.

The curves shown in Fig. 9 provide other interesting information. It will be remembered that these steels were prepared from a single heat, one part deoxidized with aluminum, furnishing a fine-grained steel, and the other not, furnishing a coarse-grained steel. The curves show the fine-grained steels to austenitize more slowly

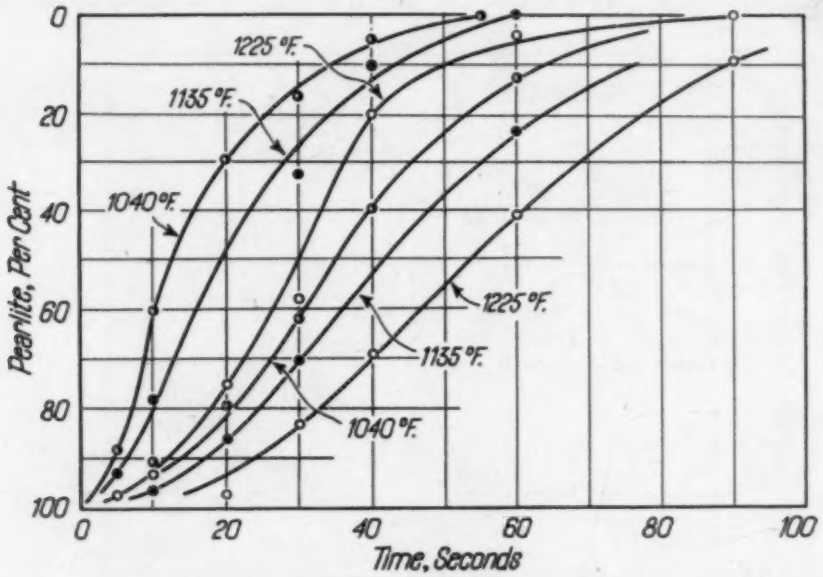

Fig. 9—Isothermal Rate of Disappearance of Pearlite Upon Austenitizing at 1350 Degrees Fahr. (730 Degrees Cent.). Three Curves to Left for "Coarse-Grained" Steel; Three Curves to Right for "Fine-Grained" Steel; Temperatures on Curves Show Temperatures at Which Initial Pearlite Had Been Formed.

than the coarse-grained steels, even when the interlamellar spacings of the initial pearlite are identical, as may be seen by comparing the three curves on the right with the three on the left. And it may be seen also that the difference is enough to preponderate over the effect of the interlamellar spacing. Calculation shows that the difference lies wholly in the rate of growth; it may be possible, though it is not certain, that these differences in the rate of growth are an effect of the excess alloyed aluminum from the deoxidation of the fine-grained steels.

Differences such as these, which are not as yet clearly understood, appear frequently among steels of nominally similar composition. Similar differences occur also for the final solution of carbide and for the final dissipation of carbon concentration gradients, and these are much in need of definitive study. It is interesting in this connection to note that pure steels austenitize far more rapidly than commercial steels.

Since, then, the rate of austenitizing varies with pearlite spacing, it will be obvious that the rate depends upon any feature of the prior treatment that affects pearlite spacing. It is well known that a fine-grained steel forms pearlite more rapidly than a coarse-grained steel, and that for this reason the cooling curve will intersect the S-curve at a higher temperature, producing a coarser pearlite at a constant rate of cooling. Accordingly, a normalized, fine-grained steel, possessing a coarser pearlite, will austenitize more slowly than a normalized coarse-grained steel of the same composition, and this is observed. It has also been observed that if the prior treatment is a quench and draw, producing a very fine dispersion of carbide, the rate of austenitizing is markedly greater than that for a pearlitic steel and greater than that for a coarsely spheroidized steel.

Rates of nucleation for austenitizing may be obtained for austenitizing curves of the type shown. It is found that there is no detectible difference in this quantity among the several curves (11), and in this connection it may be observed that there is more than ample carbide:ferrite interface for nucleation in any of the samples employed; approximation shows that there are 4×10^{11} possible sites for nucleation per cubic millimeter in the coarsest pearlite, which is 10^8 times the number of nuclei that is observed to form. It appears, at least at the present moment, that the rate of growth is the important variable in austenitizing; we shall see later that in the reverse transformation to pearlite the rate of nucleation is the important variable.

Measurements show that the rate of growth of the austenite nodule remains constant with time; it is interesting that this is true also of the rate of growth of the pearlite nodule, as we shall see. Measurements on the rate of nucleation are not very precise, but rough measurements indicate that it increases with time.

In passing, it should be remarked that segregated steels show banding upon austenitizing, as well as upon the reverse transformation to pearlite, Fig. 10. In this case it is impossible, or at least extremely difficult, to measure the rate of nucleation or the rate of growth, though the process of course is still one of nucleation and growth.

We shall have much to say later concerning the important effect of carbide and undissipated carbon concentration gradients upon the rate of formation of pearlite and upon hardenability. At the moment it will be opportune to point out the effect which they exert

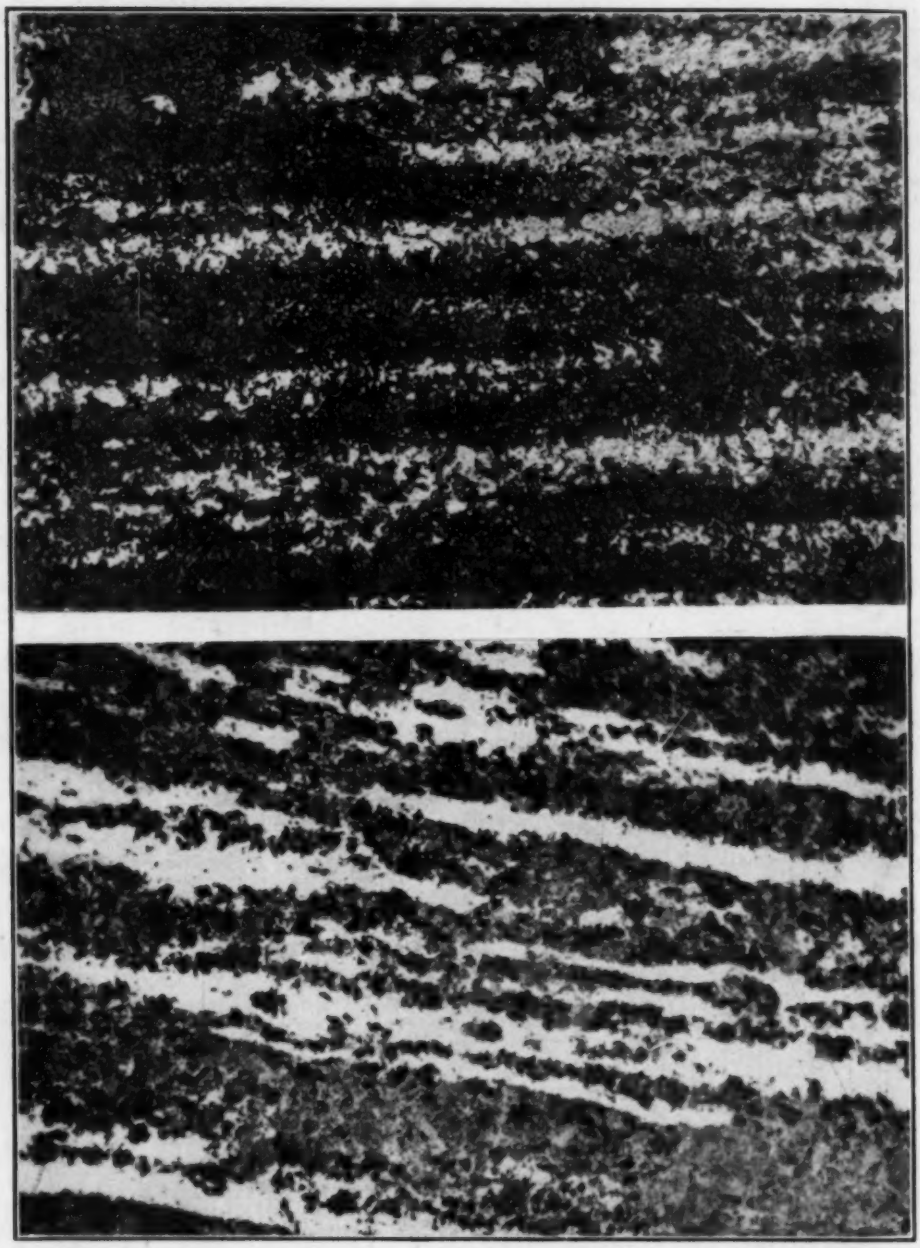

Fig. 10—Transformation "Stringers". Top—Austenite Stringers (White) in Partially Formed Austenite at 1355 Degrees Fahr. (735 Degrees Cent.). × 100. Bottom—Pearlite Stringers (Black) in Eutectoid Steel Partially Transformed to Pearlite at 1112 Degrees Fahr. (600 Degrees Cent.). × 50.

upon the structure of pearlite. By preparing samples of austenite, in one case with residual undissolved carbide, and in the other case without, Roberts (11) has been able to show that the isothermal reaction product at temperatures just below Ae_1 in the steel with undissolved carbide is not lamellar, but resembles spheroidite formed

on annealing quenched steels below Ae_1; at lower temperatures the product becomes increasingly lamellar. The product of reaction for the steel which had been thoroughly homogenized is lamellar throughout. Evidently the strong nucleating power of the residual carbide and the accompanying concentration gradients interferes with the normal growth of pearlite, producing carbide deposition on the globular carbide already present or upon carbide which come out of solution readily from points of high carbon concentration. These observations are obviously related to the recent work of Payson, Hodapp, and Leeder (18), presented here in 1939, on the spheroidizing of steel by isothermal transformation. It is now clear that the results obtained by Payson apply only to heterogeneous austenite, containing free carbide or undissipated carbon concentration gradients, or both, and it is clear also that the direct reaction product of homogeneous austenite is invariably lamellar pearlite.

The Formation of Pearlite from Austenite

Let us now consider the formation of pearlite from austenite. What we shall have to say here applies to simple-carbon steels of eutectoid composition only. It will be understood that pearlite unadulterated by free ferrite or cementite can form from austenite in hypo- or in hypereutectoid steels when reacted at low temperatures, but we are not considering such steels; nor are we considering alloy steels. In order to understand the factors which control the rate of formation of pearlite—our primary objective—it will be necessary to understand something concerning the mode of formation and the structure of pearlite.

The Mode of Formation Near Ae_1

It is a common opinion that when pearlite forms from austenite, it first appears at the austenite grain boundaries, outlining them, with the envelope thickening with time until the austenite grains are entirely consumed, Fig. 11. Such a mode of transformation may be designated as "grain-boundary transformation." This opinion has doubtless been formed from the familiar appearance of pearlite in a sample quenched at a velocity slightly less than the critical quenching velocity, or in a gradient-quenched sample, which to be sure amounts to the same thing. Since the pearlite in such samples forms

at temperatures near that of the knee of the S-curve, this mode of formation is of course characteristic of transformation near the knee, but it is not characteristic of transformation at higher temperatures, at temperatures near Ae_1, as Hull will show in a paper presented tomorrow (19).

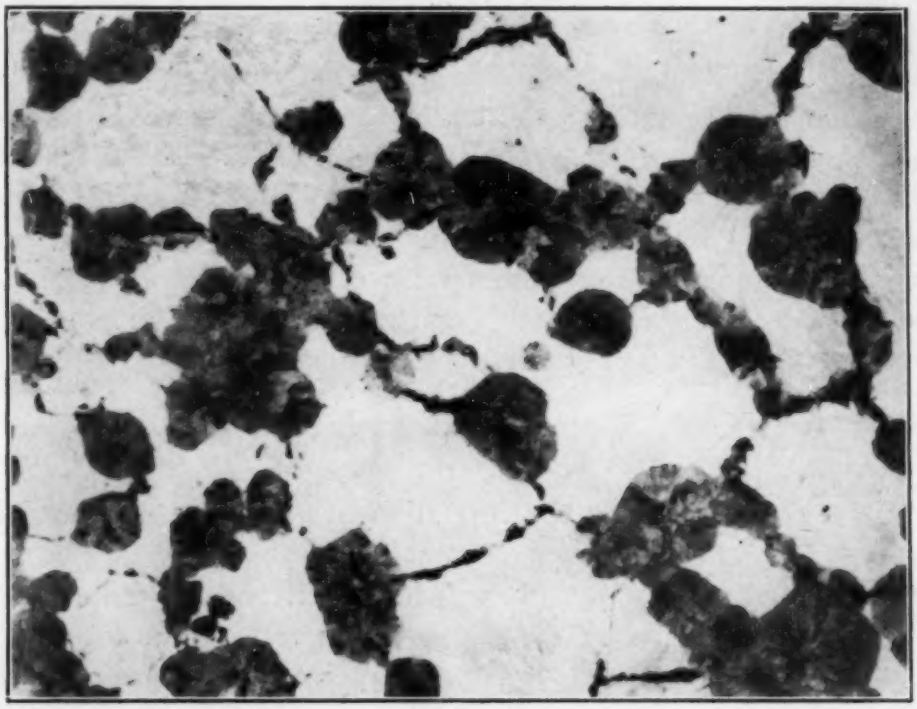

Fig. 11—Grain-Boundary Transformation in Eutectoid High-Purity Steel. Specimen Quenched from 1470 Degrees Fahr. (800 Degrees Cent.). Etched with Nital. × 100.

At temperatures near Ae_1, Fig. 12, pearlite nucleates preferentially at the austenite grain boundary, but the nodules grow very large, transgressing grain boundaries and thus growing into and across grains not yet nucleated, absorbing many austenite grains before impinging upon another growing nodule. Here evidently there are fewer effective nuclei than there are grains of austenite. This mode of formation appears general, for it has been found in all of a number of divers simple-carbon eutectoid steels—and in hypo- and hypereutectoid steels as well; for some reason it has hitherto escaped observation. This large nodule has been named the "group nodule," implying that it consumes a group of austenite grains during its growth, and the mode of transformation may be designated as "group-nodule transformation" (19).

The group nodule nucleates preferentially at the austenite grain

boundary, as shown by the fact that in partially transformed steels the first visible nodules occur at the grain boundary, and by the further fact that the rate of formation of pearlite in the temperature range where group nodules form varies with grain size. Indeed

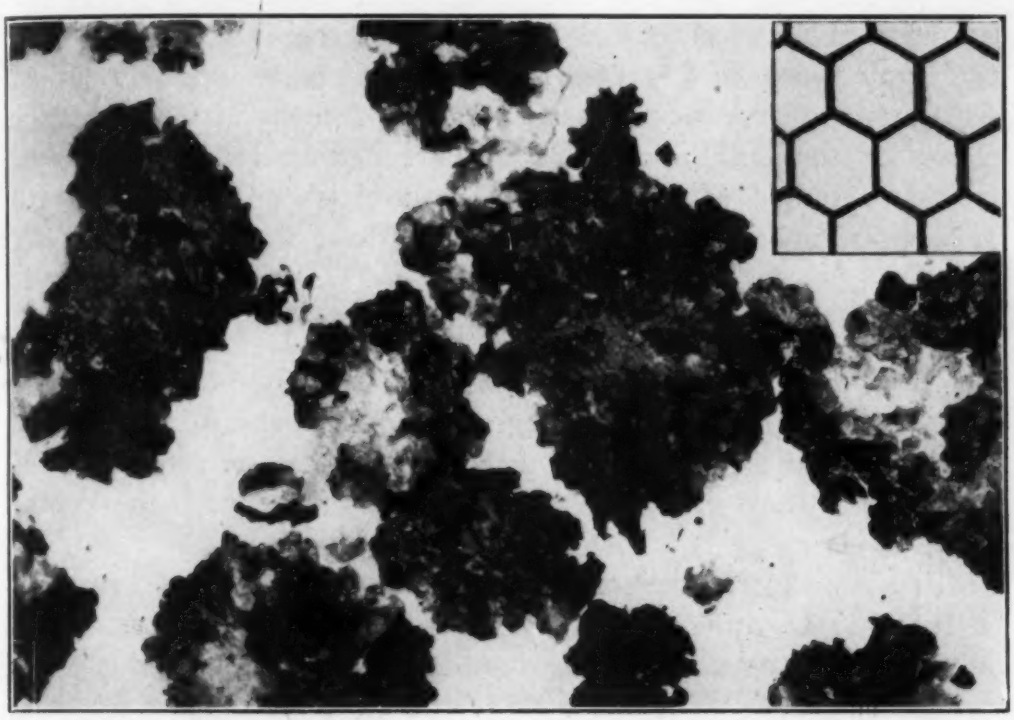

Fig. 12—Group Nodule Transformation in Eutectoid Steel. Reacted to Pearlite at 1256 Degrees Fahr. (680 Degrees Cent.) for 9 Minutes. Austenite Grain Size Shown by Sketch at Upper Right.

preferential nucleation at grain boundaries seems invariable in polyphase reaction, and there are excellent theoretical reasons for it. It is not to be implied that nuclei never form within the grain from homogeneous austenite, but merely that the rate of nucleation within the grain is extremely small compared to the rate of nucleation at the grain boundary.

The growth of a nodule across the grain boundary is doubtless similar to that occurring to a less marked degree at temperatures near the knee of the S-curve; it seems to operate as a chain-nucleation reaction, with the volume increase accompanying the formation of pearlite producing a strain which nucleates pearlite in the austenite grain lying just ahead in the path of growth.

The essential factor in the formation of group nodules appears to be a rate of nucleation very low relative to the rate of growth.

With growth across austenite grain boundaries possible, one nodule can grow very large before it impinges upon another growing nodule. The nodules grow to approximate spheres, and it may be seen that this mode of formation is very similar to that depicted in Fig. 3, and we may conclude that the principles determining the form of the isothermal curve for the formation of group nodules are identical with those already described for the reverse transformation, the formation of austenite from pearlite. And as in that case, the course of the isothermal reaction curve can be readily calculated from an assumed or measured rate of nucleation and rate of growth of spherical nodules, as Johnson and Hull have shown (9), (20).

The Mode of Formation Near the Knee of the S-curve

As we all know well, near the knee of the S-curve, pearlite nucleates rapidly at the austenite grain boundary, and in a very short time the grain is outlined and enveloped in fine pearlite, Fig. 11. Subsequent transformation consists in growth toward the center (22).

It has ordinarily been assumed that the pearlite nodule, forming at the austenite grain boundary near the knee of the S-curve, grows only into the grain that gave birth to the original nucleus and not into contiguous grains. There is good crystallographic support for such an assumption as Smith has shown (21), but as in the case of group nodules, trans-boundary growth seems to occur (though to a far less marked degree), for the half-spherical nodules formed in adjoining grains are too frequently juxtaposed, forming full spheres, to have occurred purely by chance. This behavior is again probably to be ascribed to the nucleating effect of the strain generated by the formation of the first nodule.

In each austenite grain numerous small pearlite nodules form. A nodule forms at an austenite grain boundary and starts its growth inward; before it has grown very far, however, another nodule forms close to it, and shortly the two nodules meet; continued growth then consists in the parallel growth of these two typical nodules toward the center of the grain, producing a structure somewhat similar to the columnar structure formed at the ingot wall in the freezing of a pure metal (22), (9). Here evidently the rate of nucleation is large relative to the rate of growth. The average nodule is much smaller than the austenite grain.

The explanation for the difference between the mode of transformation near Ae_1 and that near the knee of the S-curve appears then to be this: At high temperatures the rate of nucleation is small compared to the rate of growth, and a few large nodules form; at low temperatures the rate of nucleation is high relative to the rate of growth, and many small nodules appear (19), (20). In the former case the final nodule in general is much larger than the

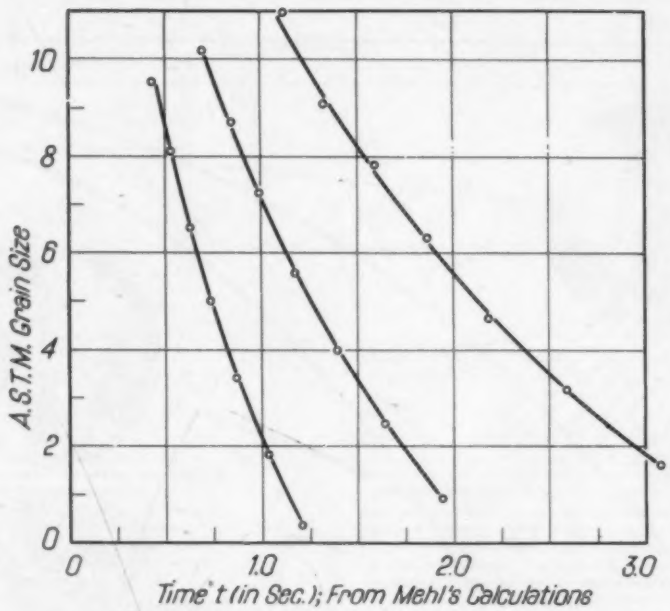

Fig. 13—Grossmann's Calculation of Relation Between Grain Size and Time for the Formation of 50 Per Cent Pearlite (Ref. 23) Used as Basis for Evaluating the Effect of Grain Size Upon Hardenability.

austenite grain, and in the latter always much smaller. It is obvious that neither nodule size may be taken as the austenite grain size; Vilella has been quite clear on this point though others have occasionally been confused.

It is obvious from the appearance of a sample reacted near the knee that the rate of nucleation within the grain is extremely low, and this appears always to be true of homogeneous austenite. It is the low rate of nucleation within the grain together with a rate of nucleation at the grain boundary high compared to the rate of growth, that causes the austenite grain boundary to be clearly outlined and enveloped on partial transformation near the knee, and it is this that enables us to determine the austenite grain size by a gradient quench. But austenite is sometimes not homogeneous, and

heterogeneous austenite—austenite containing free carbide—frequently provides a high rate of nucleation within the grain, and in this case—a case fairly frequently met as we shall see—it is impossible or at least difficult to determine the austenite grain size by a gradient quench.

The course of the isothermal reaction curve for grain boundary transformation can be readily calculated from an assumed or measured grain size, a rate of nucleation, and a rate of growth, though

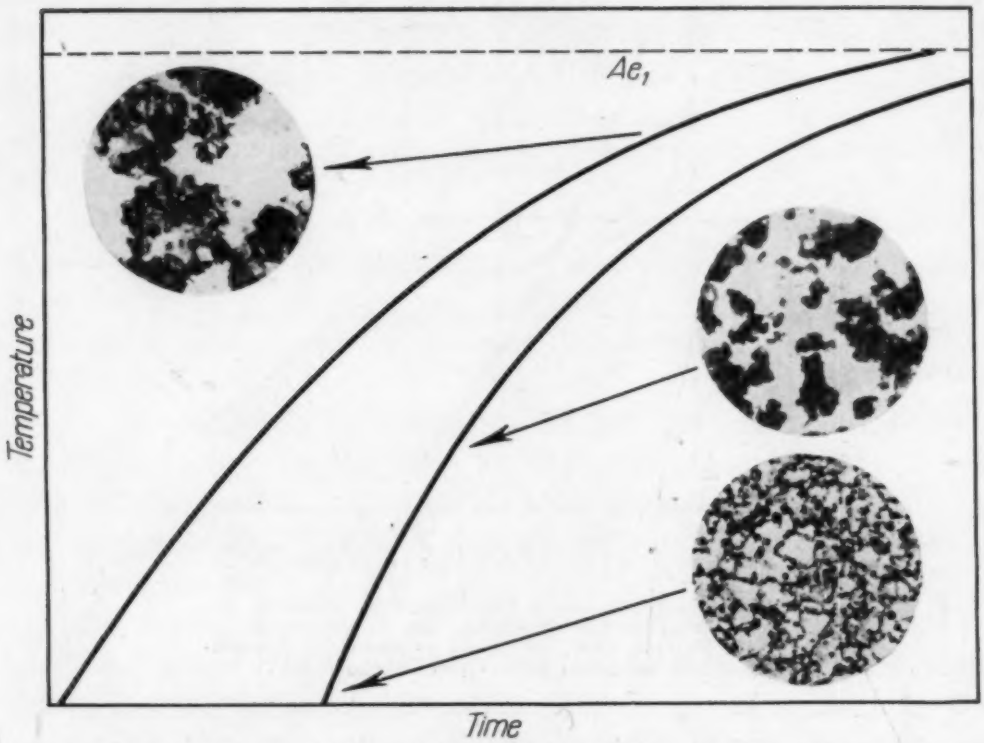

Fig. 14—Showing Modes of Formation of Pearlite at Different Temperatures Correlated with S-Curve. Group Nodule Transformation Near Ae_1, Grain-Boundary Transformation Near Knee, Intermediate Mode at Intermediate Temperature.

since the mode of formation is different from that for group nodule transformation obtaining near Ae_1, the form of the calculation is different (9), (22).

Such calculations are of real value in the study of the decomposition of austenite. If one of the variables, say the rate of nucleation, is unknown, it can be calculated from the other variables and the reaction curve. Some of the data presented later were obtained in this way; they could not have been obtained otherwise. The three variables determining the isothermal reaction curve are: the rate of nucleation per unit area of the grain boundary surface, the grain

size, that is, the extent of the grain boundary surface, and the rate of growth. If the latter two are held constant and only the grain size varied, the effect of this upon the isothermal reaction curve can be calculated. Grossmann (23), Fig. 13, applied the analysis in this way to the reaction precisely at the knee of the S-curve, and employing these relative rates, was able to predict the effect of grain

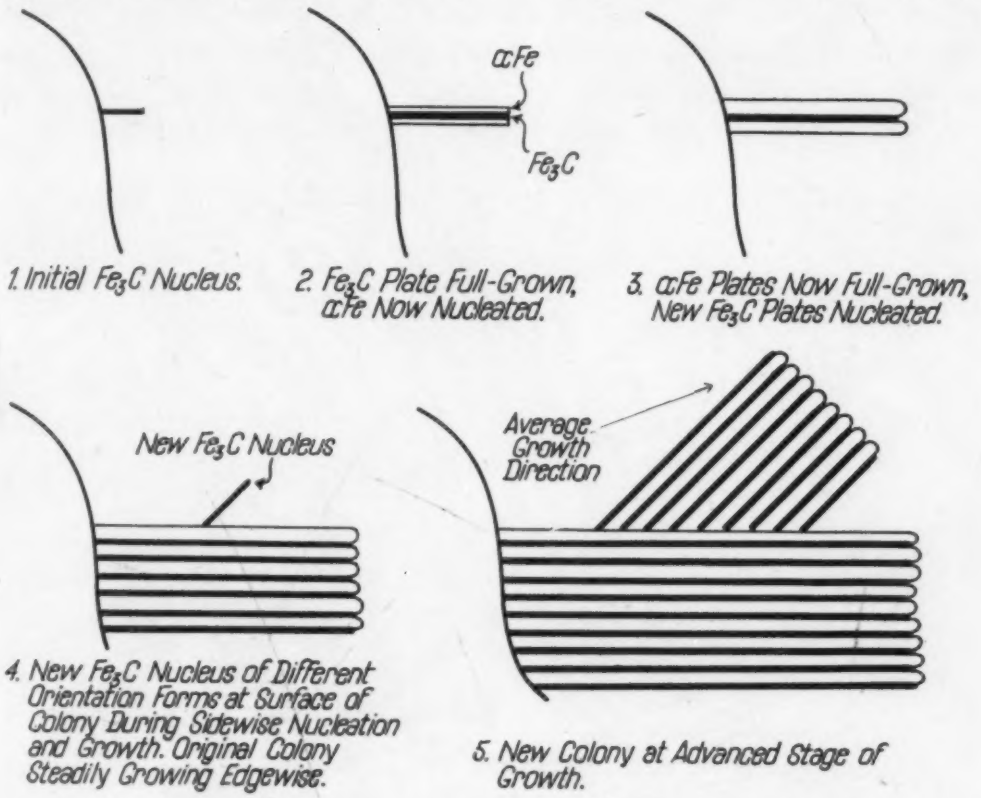
αFe
Fe3C
1. Initial Fe3C Nucleus.
2. Fe3C Plate Full-Grown, αFe Now Nucleated.
3. αFe Plates Now Full-Grown, New Fe3C Plates Nucleated.
New Fe3C Nucleus
4. New Fe3C Nucleus of Different Orientation Forms at Surface of Colony During Sidewise Nucleation and Growth. Original Colony Steadily Growing Edgewise.
Average Growth Direction
5. New Colony at Advanced Stage of Growth.

Fig. 15—Diagram Showing the Nucleation and Growth of Pearlite Lamellae.

size alone upon the depth of hardening, and carrying the analysis one step further, was able to predict the effect of grain size in steels of different hardenabilities. The predicted results are in very close agreement with depths of hardening actually observed.

We thus have two extremes in the mode of transformation, the group nodule transformation at high temperatures, near Ae_1, and the grain boundary transformation at low temperatures, near the knee of the S-curve. Between these two extremes graduated intermediate structures, varying in nodule size from one extreme to the other, are observed, Fig. 14. The temperature at which the change from one type to another occurs varies somewhat with grain size, and can be calculated as a function of grain size.

Pearlite Colonies—Nucleation and Growth of Pearlite Colonies

I have spoken thus far of the pearlite nodules with but little regard for their structural constitution. Each pearlite nodule, whatever the temperature at which it forms, is composed of smaller units, the so-called "pearlite colonies" of Belaiew (24). Proper attention to these is necessary if the genesis and growth of pearlite nodules is to be understood.

Good reasons can be advanced for assuming that pearlite is

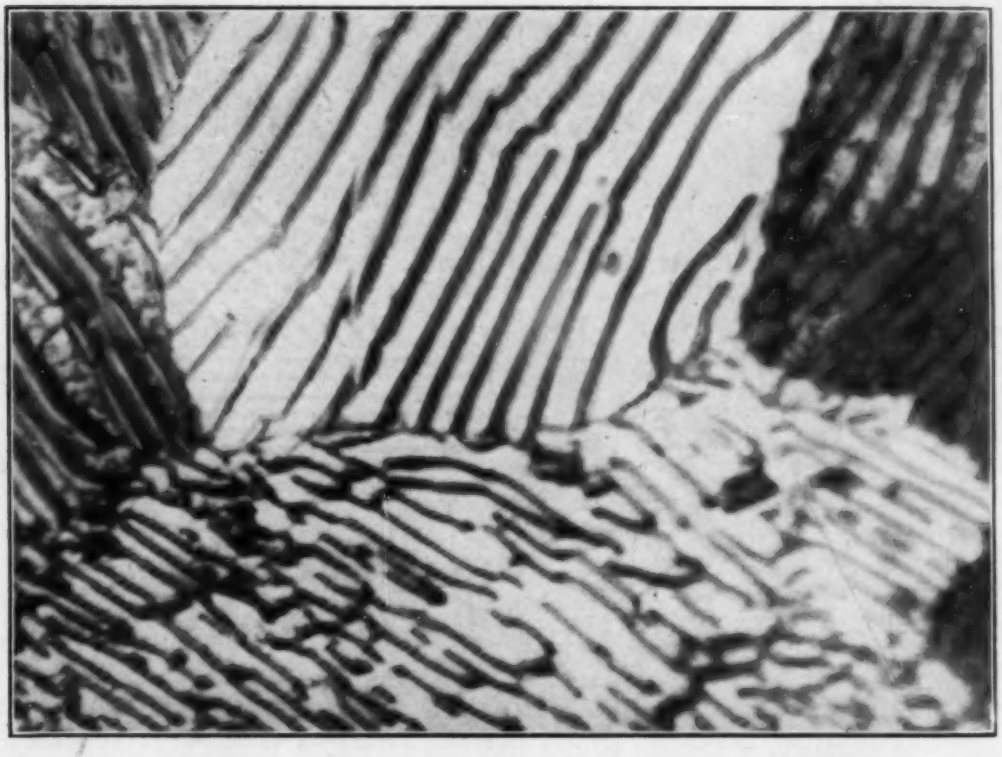

Fig. 16—Pearlite Colonies in Eutectoid Steel. Transformed at 1320 Degrees Fahr. (715 Degrees Cent.). Electrolytically Polished. Vilella's Etch. × 2500.

nucleated by cementite (22), Fig. 15. The original cementite plate nucleus grows, diminishing the carbon content of the contiguous austenite until a plate of ferrite forms lying parallel to and against it. This alternating process continues, building a lamellar structure which once established by this sidewise nucleation then grows edgewise. This packet of lamellae is a pearlite colony. The ferrite in the colony, and presumably the cementite also, has a simple orientation, as may be shown by suitable etching (19), Fig. 16. Occa-

sionally, metallographers have been tempted to identify the size of the pearlite colony, as shown by the area of parallel lamellae or as disclosed by colors under polarized light, as the size of the austenite grain, but this is incorrect. Colonies are always smaller than the austenite grain and usually very much smaller.

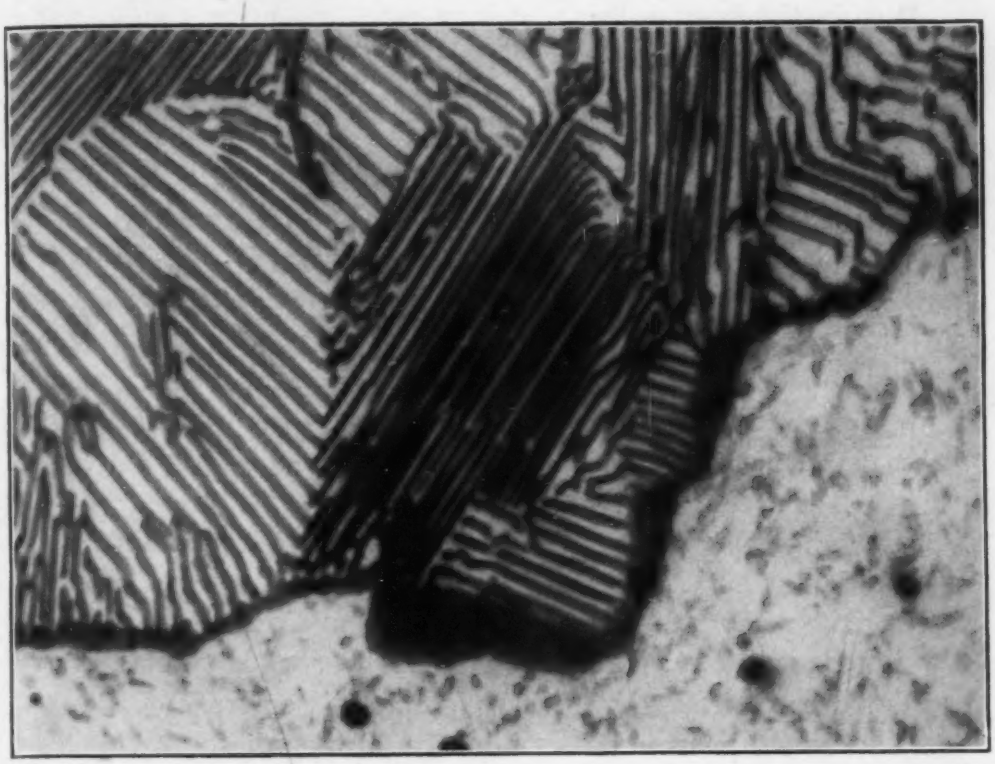

Fig. 17—Pearlite Colonies. In Eutectoid Steel Partially Transformed at 1290 Degrees Fahr. (700 Degrees Cent.). Growth of Nodule in Direction of 5 O'clock. Electrolytically Polished. Vilella's Etch. × 2500.

After a time period some circumstance, possibly the strain which the reaction produces, creates a new plate nucleus of cementite, differently oriented from the first, which then grows by the process described and becomes the progenitor of a new pearlite colony, Fig. 17. The direction of the lamellae is not necessarily in the direction of over-all growth, though this appears favored.

Thus, a nodule is composed of the successive growths of colonies (19); the advancing nodule interface is a serrated face of numerous individual colonies. When group nodules form, crossing austenite grain boundaries during growth, the process is the same; when the nodule during growth reaches an austenite grain boundary, new colonies are initiated across the austenite grain boundary; this is the chain-nucleation process mentioned above. Ap-

parently the grain boundary does not offer an effective impediment to growth, for it will be shown that the rate of growth does not vary with austenite grain size.

The Nodular Troostite Controversy

We should now, I think, devote some attention to the nature of pearlite formed at the knee of the S-curve, for as we know it is the rate of formation of pearlite at this point that determines hardenability. It has, of course, been known for some time that the interlamellar spacing in pearlite decreases steadily as the temperature of formation decreases. An extended series of precision measurements of the interlamellar spacing in a number of plain-carbon and alloy steels is being presented at this meeting by Pellissier, Hawkes, and Johnson (25). As the reaction temperature is lowered, a product is obtained where the microscope can resolve only part of the nodule, and when the temperature of formation is that of the knee of the S-curve a product is obtained which frequently cannot be resolved in any part. Metallurgists have ordinarily been content to think that those portions which are not resolved by the microscope are nevertheless lamellar pearlite, but of an interlamellar spacing too small for the resolution of the metallurgical microscope. Kourbatoff (26) and Benedicks (5) held this view in 1905, as have many metallurgists since; yet there have been vigorous dissenters.

If we are to provide direct evidence on this question, we clearly need some method of observation providing a markedly greater degree of resolution than that characteristic of the best of metallurgical microscopes, and such a method is now available. During the last few years the electron microscope, operating on electron-optical principles, has been developed which is capable of yielding a degree of resolution for transparent substances up to 100,000 diameters magnification comparable, roughly, to that of the light-optical microscope at 1500-2500 diameters. This microscope will resolve distances as small as 100-150 Å and has even made it possible to "see" large organic molecules. I shall show the first results of the application of the electron microscope to the study of steel, obtained in conjunction with our studies of pearlite. This work has been done during the last two years in cooperation with Dr. Zworykin of the Radio Corporation of America and his associates Drs. Ramberg and Baker, employing the type of microscope and the technique which they have developed.

Application of the Electron Microscope

The electron microscope operates on the principle that a beam of electrons may be spherically diverted on passing through a magnetic coil, in a manner analogous to the refraction which light waves suffer on passing through a lens, producing an analogous magnification. With a suitable system of such magnetic lenses, an electron beam may be passed through a sample transparent to it, and a greatly magnified image obtained which may be viewed on a fluorescent screen or photographed.

Metal samples, however, cannot be used directly on the present form of the electron microscope, for in usable sections they are opaque to the electron beam as they are to light. Reflection methods as employed in the metallurgical microscope are not available, and a different solution to the problem is necessary. This is found in the replica method adopted.

The technique in its present form consists in preparing a sample by the usual metallographic means and etching it in a manner which gives the best results on viewing under the metallurgical microscope at the highest magnifications, for at the moment it seems that this degree of etching is optimum also for this new purpose; this sample is then coated with a layer of silver 0.1 mm. thick, deposited upon it by evaporation from massive silver; this layer is stripped from the sample, its under surface bearing a minutely accurate contour replica of the surface of the sample. Upon this silver replica is placed an extremely thin layer of collodion and the silver removed from it by solution in acid, yielding then a second replica, now a positive of the original steel surface. This thin second replica is then placed in the electron microscope and photographed, Fig. 18.

Now the transmission electron-photomicrograph of the collodion replica obtained is one in which the high spots on the original sample appear dark, for the collodion replica is thick there, and the low spots light, for the replica is thin at such points. The result is a contour photograph, differing in appearance somewhat from the ordinary photograph, losing some of its advantages, gaining others, and of course gaining greatly in magnification and resolution. With pearlite, cementite appears dark and ferrite light, as they do in ordinary photomicrographs.

Fig. 18 is an electron microscope photomicrograph at a magni-

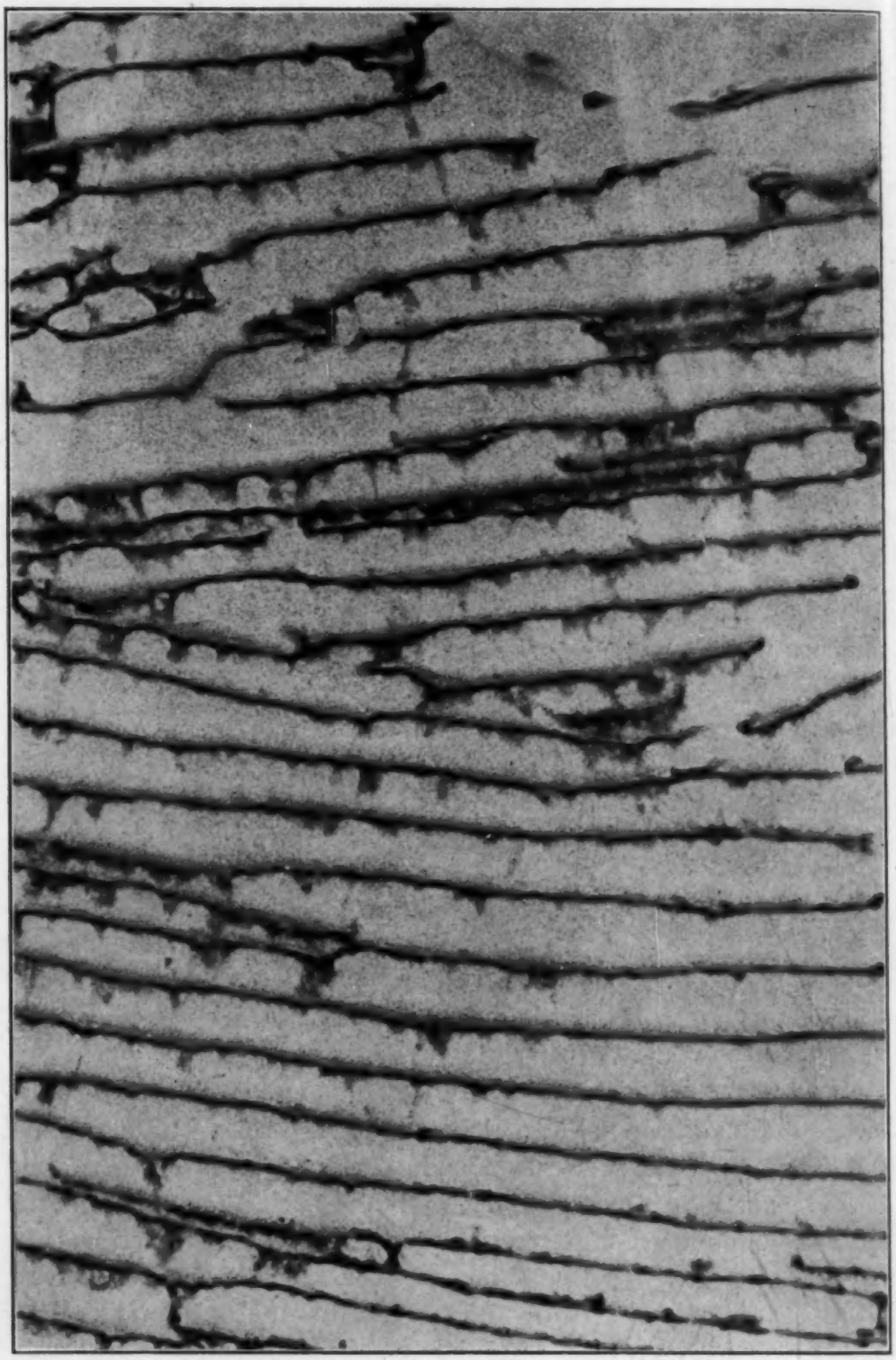

Fig. 18—Electron Microscope Photomicrograph of a Sample of Pearlite Formed Isothermally at 1180 Degrees Fahr. (640 Degrees Cent.), Electrolytically Polished, Etched with Picral. × 25,000.

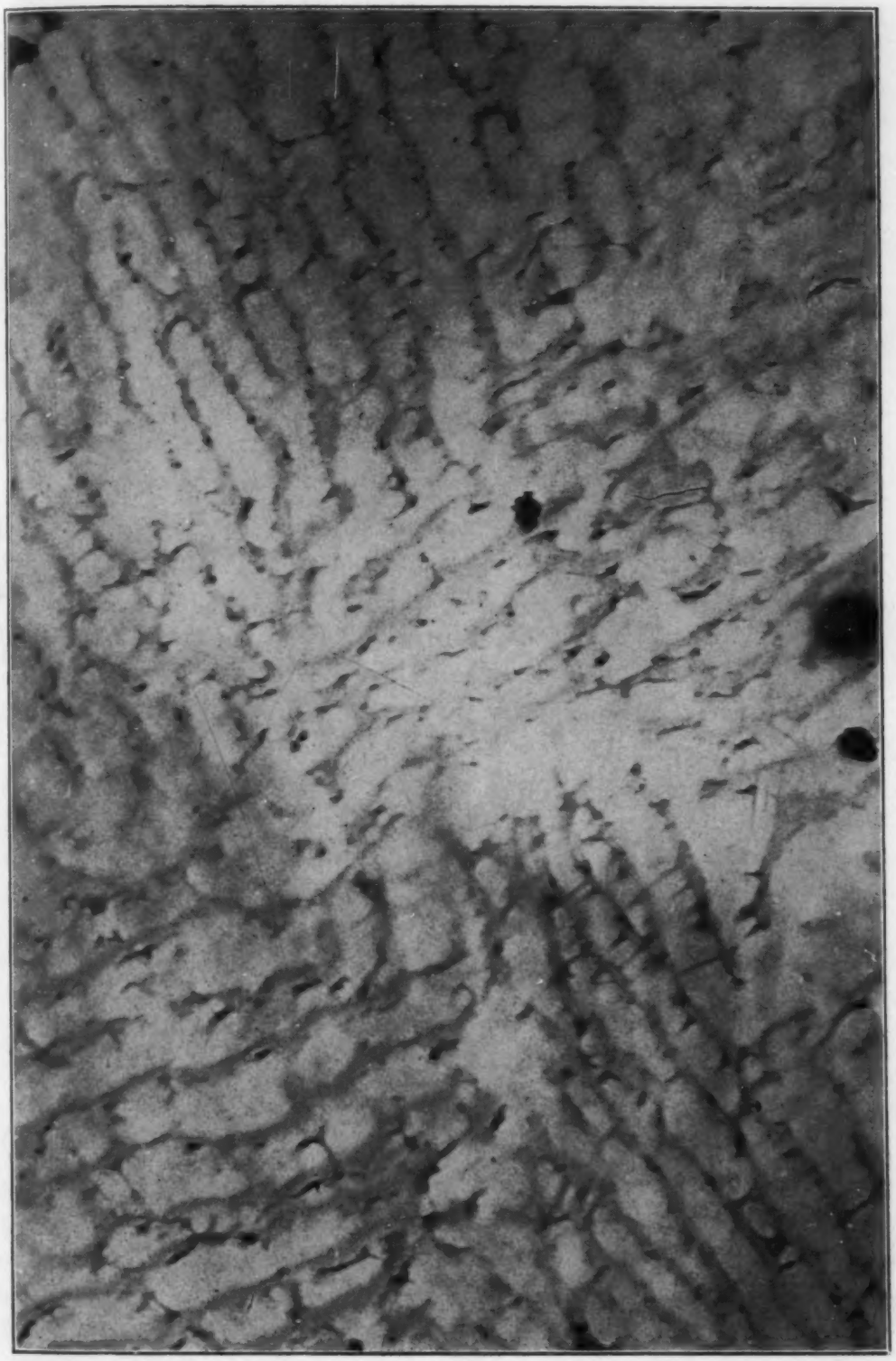

Fig. 19—Electron Microscope Photomicrograph of Same Sample of Pearlite as Used in Fig. 18 Showing a Somewhat Finer Apparent Spacing. The Large Black Spots are Spots of Silver Left Undissolved on the Collodion Replicas. × 25,000.

fication on the original photomicrograph of 25,000 diameters of a sample of pearlite formed isothermally at 1180 degrees Fahr. (640 degrees Cent.); this pearlite is not entirely resolved by the ordinary microscope, though the electron microscope resolves it wholly. The photomicrograph is typical of the best that have been obtained. Fig. 19 at the same magnification, is from the same sample, showing a somewhat finer apparent spacing. The large black spots in this slide, and those in later slides, are to be disregarded: they are spots of silver left undissolved on the collodion replicas; they offer little risk in interpreting the photomicrograph and are of help in focusing.

Fig. 20, at 30,000 diameters, of a pearlite formed at 1075 degrees Fahr. (580 degrees Cent.) shows an effect which has frequently been noted in very fine pearlites, an effect which appears to become more pronounced as the temperature of formation is decreased, namely, that the cementite occasionally seems to bridge the lamellae, i.e., occasionally to cross-connect one cementite layer with the next.

Fig. 21 shows a pearlite formed at 1100 degrees Fahr. (595 degrees Cent.), at a magnification of 30,000, which demonstrates the resolution that can be attained on pearlite; the spacing shown—the photomicrograph could doubtless be improved—is the smallest that has been found. This sample and many others—some 200 electron microscope photomicrographs of steel have now been made—show that there are no areas in a sample composed of what we have so frequently called nodular troostite that cannot be resolved into lamellar pearlite, and accordingly it appears a reasonably safe conclusion that nodular troostite is in fact pearlite of a very small interlamellar spacing.

We are, then, evidently resolving structures which the ordinary microscope cannot resolve. The question of degrees of resolution inevitably arises, and as you know, there is room for controversy. In order to be able to express comparative degrees of resolution, I have obtained a selection of the best photomicrographs of nodular troostite taken by others through the years with the ordinary microscope, and I have measured the minimum spacing which could be resolved; this spacing is approximately 860 Ångström units, or 3.4 millionths of an inch. Similar studies on the photomicrographs of pearlitic nodular troostite taken on the electron microscope provides a minimum spacing of 300 Å or 1.2 millionths of an inch, and it thus appears that a new degree of resolution has been attained. I do not think that this is quite the limit for the electron microscope

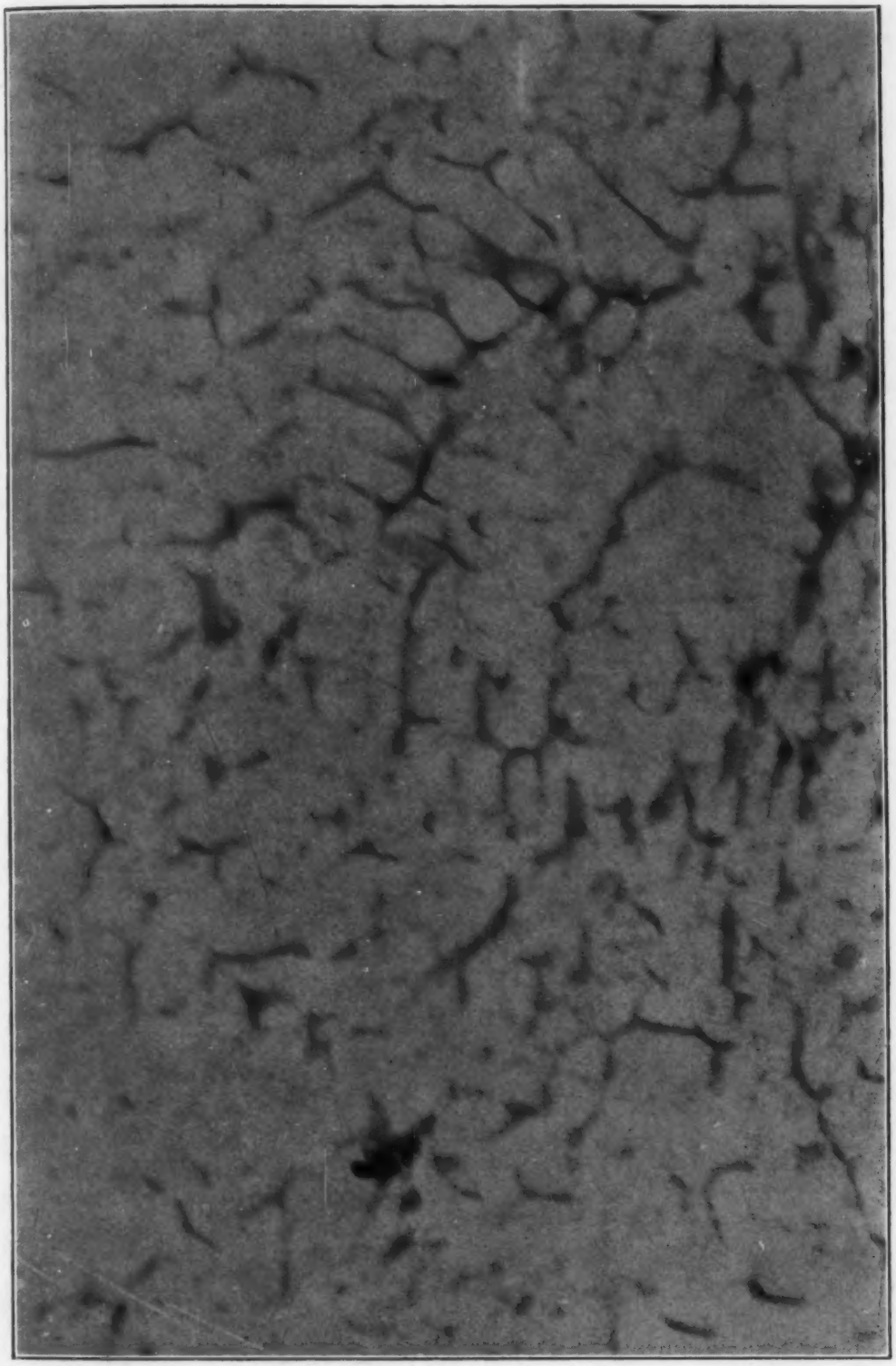

Fig. 20—Electron Microscope Photomicrograph of a Sample of Pearlite Reacted Isothermally at 1075 Degrees Fahr. (580 Degrees Cent.) Showing "Bridging" of Cementite Lamellae. × 30,000.

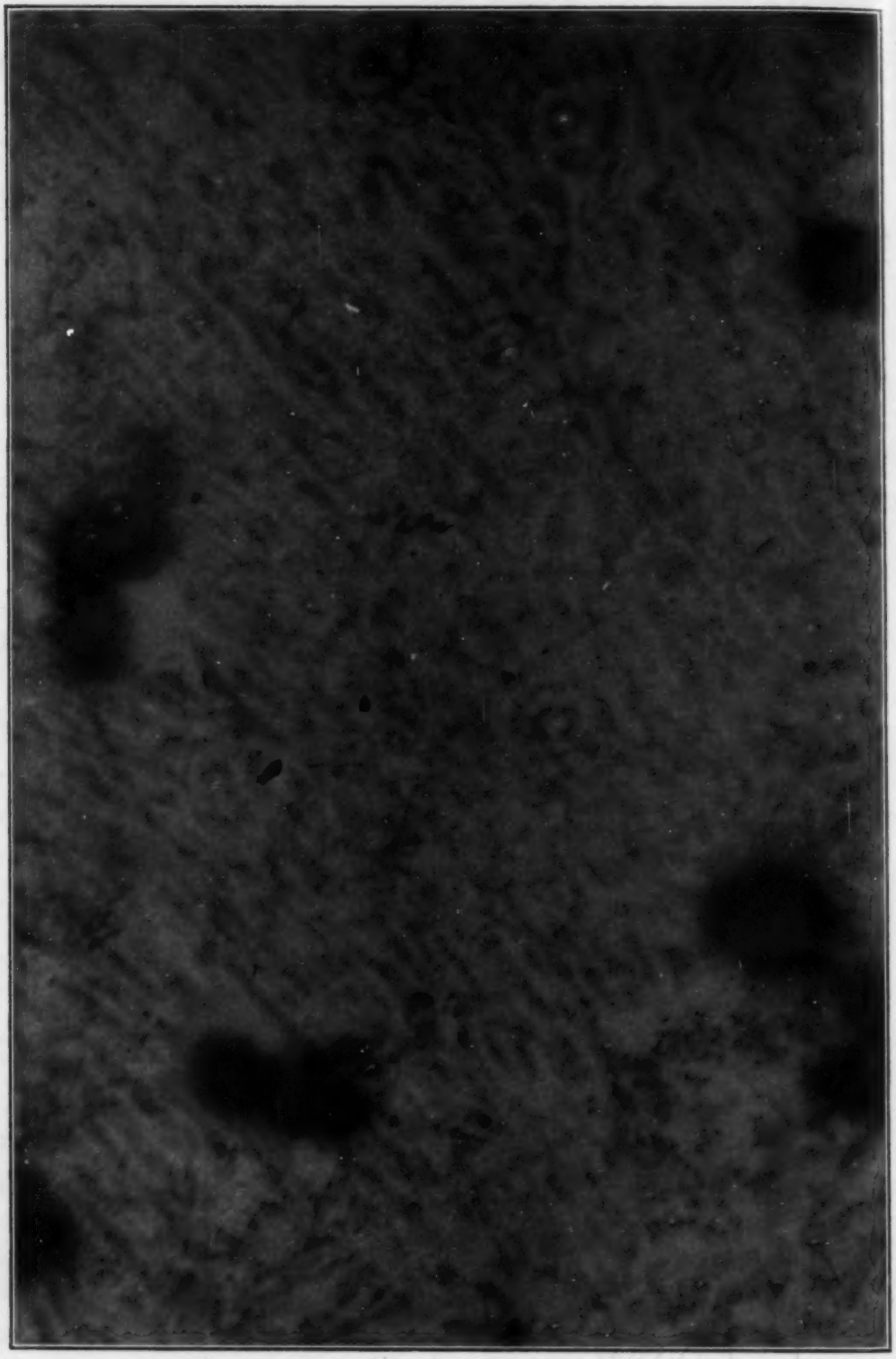

Fig. 21—Electron Microscope Photomicrograph of Pearlite Formed Isothermally at 1100 Degrees Fahr. (595 Degrees Cent.). × 30,000.

for I shall show evidence of superior resolution in a moment: the spacing of 300 Å appears to be merely the smallest interlamellar spacing exhibited by the samples of nodular troostite.

Samples of upper bainite provide very sharp electron microscope photomicrographs, as shown in Fig. 22, taken at 18,500 diameters. Here the light ferritic areas are clearly defined, but it is interesting to note that no clear registration of carbide particles is obtained.

As a final demonstration of the possibilities of this technique, we may view an electron microscope photomicrograph, Fig. 23, of a martensite tempered one hour at 930 degrees Fahr. (500 degrees Cent.) which gave a structure which under the ordinary microscope was very poorly delineated, to say the least. The electron microscope photomicrograph, at a magnification of 50,000 diameters, shows light-shaded islands of ferrite and what appears to be a fine carbide dispersion (though I am not certain that it is), with particles 0.8 mm. apart on the photograph at 50,000 diameters clearly resolved, equivalent to an absolute distance of 150 Å or approximately 50 atom diameters.

This technique is of course new, and one should be conservative in making claims for it, yet it does seem that it provides a new degree of resolution, and it seems also to have given an answer to the nodular troostite controversy.

The Rate of Formation of Pearlite from Austenite

The Rate of Growth. With this background of the structure and the mode of formation of pearlite, let us then consider the factors which determine the rate of formation of pearlite. Of the two variables determining the rate of formation of pearlite, namely, the rate of nucleation and the rate of growth, the rate of growth is far less subject to change through alteration in structure, and through minor variations in composition than the rate of nucleation. It will be convenient to consider it first, then to set it aside, devoting most of our attention to a consideration of the rate of nucleation.

The rate of growth is measured by plotting the diameter of the pearlite nodule as a function of time, which provides a curve, the slope of which is the rate of growth (20), Fig. 24. It is an interesting and important fact that this plot is a straight line, as Hull has shown for a number of commercial steels. This curve is for growth near Ae_1, and it is clear from the diagram that the rate of

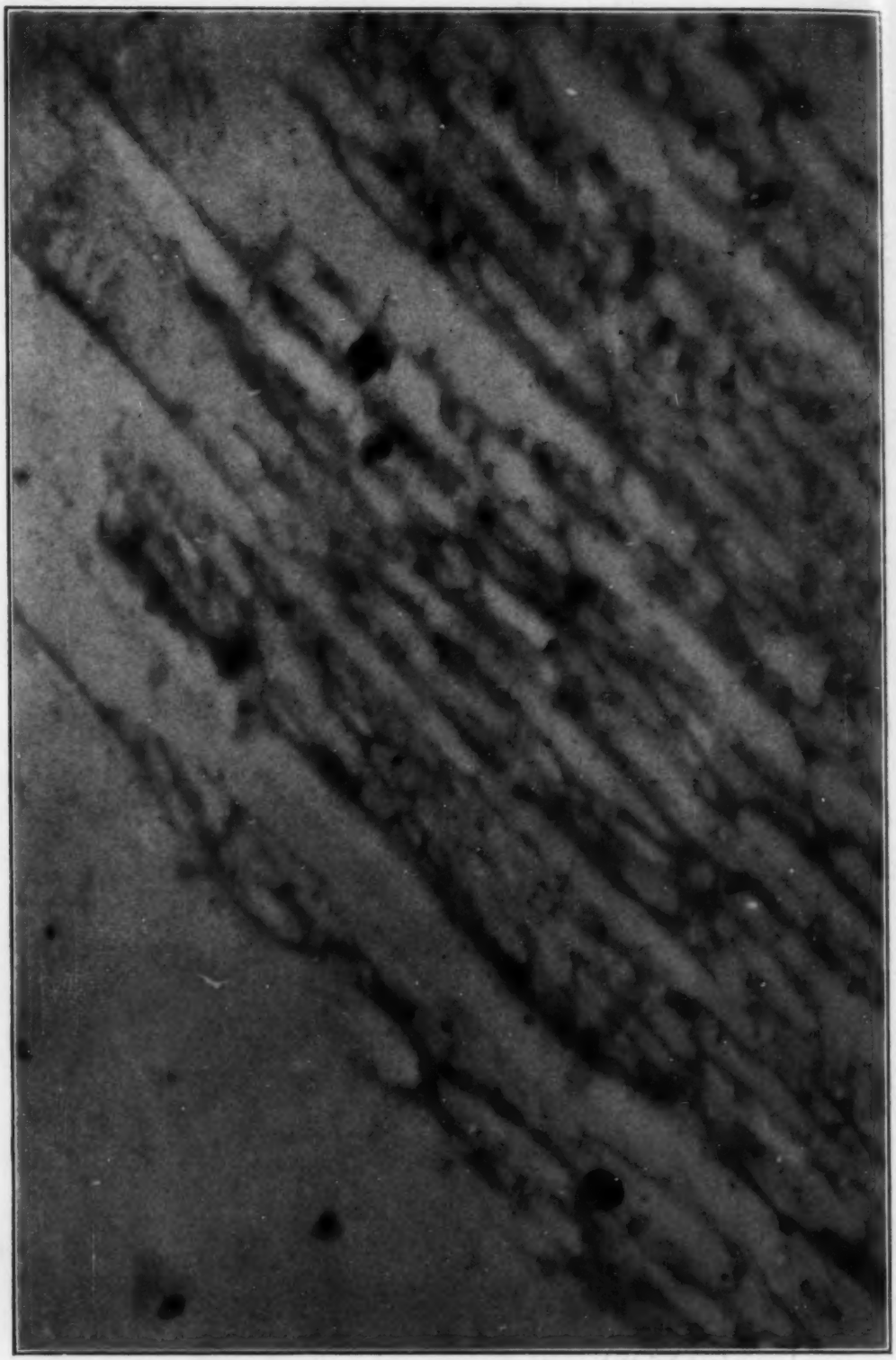

Fig. 22—Electron Microscope Photomicrograph of a Sample of Bainite Formed Isothermally at 860 Degrees Fahr. (460 Degrees Cent.). Etched with Nital. × 18,500.

Fig. 23—Electron Microscope Photomicrograph of Martensite Tempered One Hour at 930 Degrees Fahr. (500 Degrees Cent.). Etched with Picral. × 50,000.

growth in this temperature range does not vary with time. It is unfortunately impossible to measure the rate of growth as a function of time at temperatures near the knee of the S-curve, for the rate of reaction is too rapid to permit such measurements, but it would appear a safe assumption that here the rate of growth also does not vary with time.

In simple-carbon eutectoid steels, the rate of growth of pearlite

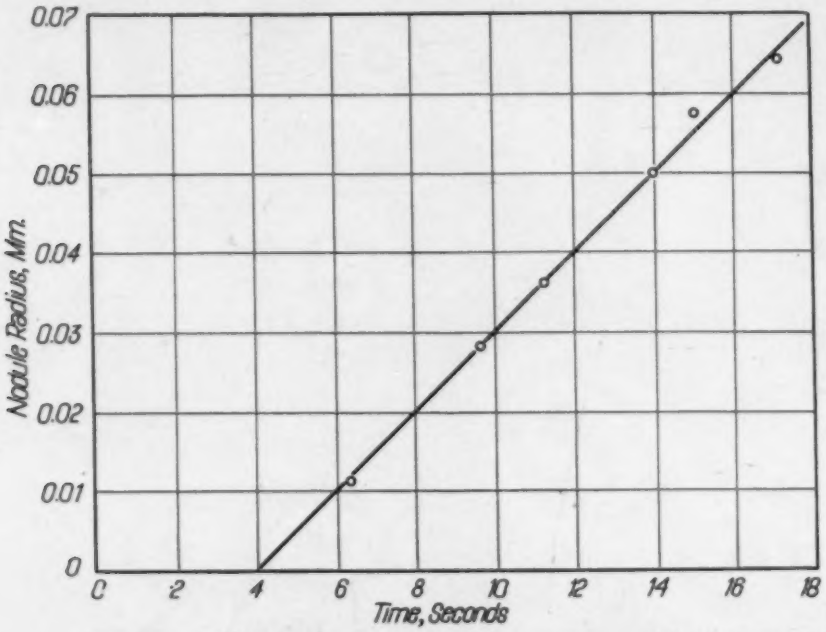

Fig. 24—Nodule Radius as a Function of Time. Eutectoid Steel Reacted to Pearlite at 1255 Degrees Fahr. (680 Degrees Cent.).

depends upon the speed at which carbon will diffuse in austenite in segregating from austenite into the lamellar aggregate of cementite and ferrite. It is manifest that this depends upon the distance between the cementite lamellae. Pellissier, Johnson, and Hawkes (25) have shown that the spacing in pearlite formed isothermally does not vary with austenite grain size, and Wells and I (27) have shown that the rate of diffusion of carbon in austenite does not vary with austenite grain size. In view of these facts, it would be expected that the rate of growth would be independent of austenite grain size, and this, in fact, has been shown to be the case for a number of steels.

Furthermore, it has been demonstrated that neither the interlamellar distance in pearlite nor the rate of diffusion of carbon in austenite are much if any affected by minor variations in purity or by deoxidation practice, a circumstance which would suggest that

the rate of growth also is not affected by these factors. There are ample data confirming this prediction; some of these are given in Table I.

Table I

Effect of Grain Size, Deoxidation Practice, and Austenite Heterogeneity Upon the Rate of Growth (20)

Steel	Austenitized ½ Hr. at	Grain Size (A.S.T.M. No.)	Transformation Temperature	Rate of Growth 10^{-3} Mm. Per Second
Fine-grained	1610° F.	7¼	1255° F.	2.2
Fine-grained	1895° F.	3	1255° F.	2.3
Coarse-grained	1345° F.	6¾	1255° F.	2.1
Coarse-grained	1615° F.	4	1255° F.	2.1
Coarse-grained	1700° F.	3	1255° F.	2.2

It is clear from this table that the rate of growth, listed in the last column, is independent of the austenitic grain size, which is listed in the middle column; since the pearlite nodule traverses austenite grain boundaries during its growth at this temperature, the lack of a dependence of the rate of growth upon grain size must mean that the nodule loses little or no time in growing across a grain boundary.

Inasmuch as the so-called "fine-grained" steel was deoxidized with aluminum and thus contained alumina and doubtless residual alloyed aluminum (17), while the "coarse-grained" steel was not deoxidized with aluminum and was therefore relatively free from these constituents, and since no appreciable differences in the rate of growth are evident in the table, it may be concluded that such variations in deoxidation practice are without effect upon the rate of growth.

Finally, it may be seen from the table that the rate of growth is independent of the state of homogeneity of the austenite, for the variations in the austenitizing times and temperatures noted are not paralleled by any variation in the rate of growth. The steel austenitized at 1345 degrees Fahr. (730 degrees Cent.) exhibited numerous undissolved carbide particles and thus represented an extreme degree of austenite heterogeneity, yet the rate of growth is not different from that for the steel austenitized at 1700 degrees Fahr. (925 degrees Cent.), which was far more homogeneous.

Data similar to these have been obtained for simple-carbon one per cent carbon steels, with wide variation in austenitizing time and temperature, and for reaction to pearlite at temperatures between

1290 and 1150 degrees Fahr. (700 and 620 degrees Cent.), with identical results. In no case does the rate of growth vary appreciably.

We thus arrive at an important conclusion: The rate of growth is a structure-insensitive property. The reasons for differences in

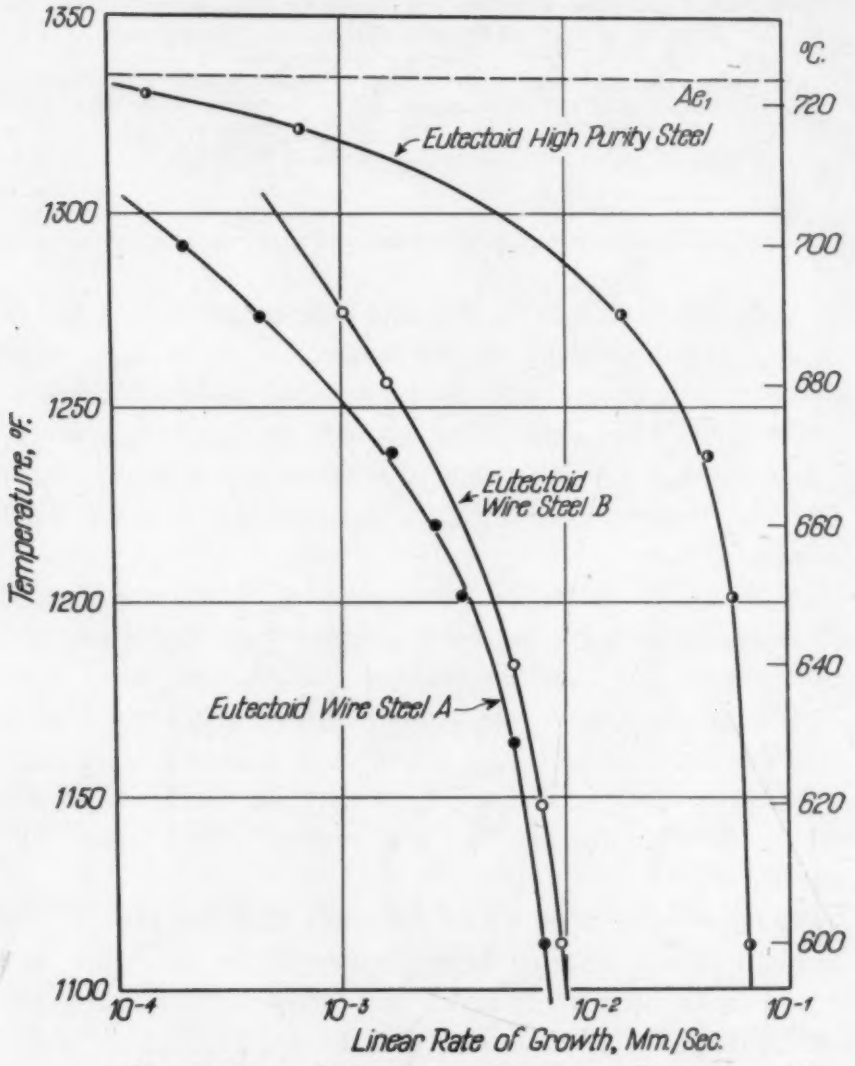

Fig. 25—Rates of Growth as a Function of Temperature of Steels as Noted on Curves.

hardenability in simple carbon eutectoid steels, depending on differences in the rate of formation of pearlite near the knee, must therefore be sought in differences in the rate of nucleation and not in the rate of growth. This fortunately simplifies the problem.

As a final question concerning the rate of growth, we may inquire how the rate of growth varies with temperature. It is a

familiar fact that the rate of formation of pearlite increases as the temperature of reaction is lowered; the many S-curves now available for simple-carbon eutectoid steels testify to this fact. As the temperature of reaction is lowered, both the rate of nucleation and the rate of growth increase. The variation in the rate of growth with temperature is shown in Fig. 25 for three simple-carbon eutectoid steels (20), (28), two of which are commercial steels, and one a high purity steel. It may be seen that the rate rapidly increases with decreasing temperature. Similar curves of the rate of growth for other steels and for hypo- and hypereutectoid steels are now available.

The values near the knee of the S-curve, in the neighborhood of 1060 degrees Fahr., are affected by recalescence, rendering the recorded values somewhat too low. The specimens employed, however, were $\frac{3}{32}$ inch in section or less, and though all steels are rapidly reacting, the amount of recalescence occurring when reaction was performed near the knee in a well-stirred and clean lead bath is so little that the reaction takes place at a temperature not more than 10 degrees Fahr. above the bath temperature, and there is no measurable temperature rise during reaction. The recent criticism by Lange (29) of the work of Bain and his colleagues and of the inferences I drew from it several years ago (22), on the basis of extensive distortion of reaction rates by recalescence cannot be maintained, for the recalescence under these conditions (and those of Bain) is very minor. Lange, surprisingly, reacted samples in still air, a treatment hardly likely to minimize recalescence.

Variations in alloy composition exercise distinct effects upon the rate of growth. Analysis of a large body of data in a number of simple carbon eutectoid steels shows the rates of growth to be the same if the manganese contents are equal and to decrease as the manganese content is increased, but these variations are relatively minor; this appears to be the reason for differences among the curves shown in Fig. 25. Alloy steels, which we are not considering here, represent a different case; appreciable quantities of alloy change the rate of growth appreciably, usually decreasing it, but in the case of the anomalous cobalt steels actually increasing it, as Hawkes has been able to show (30).

The Rate of Nucleation. It is clear then that the rate of growth is remarkably little affected by ordinary variations in composition and structure of simple-carbon eutectoid steels. But this is by no

means true of the rate of nucleation, for the rate of nucleation is a property which is extremely structure-sensitive, as we shall see in considering the data. Variations in the rate of formation of pearlite throughout its temperature range originate in variations in the rate of nucleation, and since hardenability depends upon the rate of

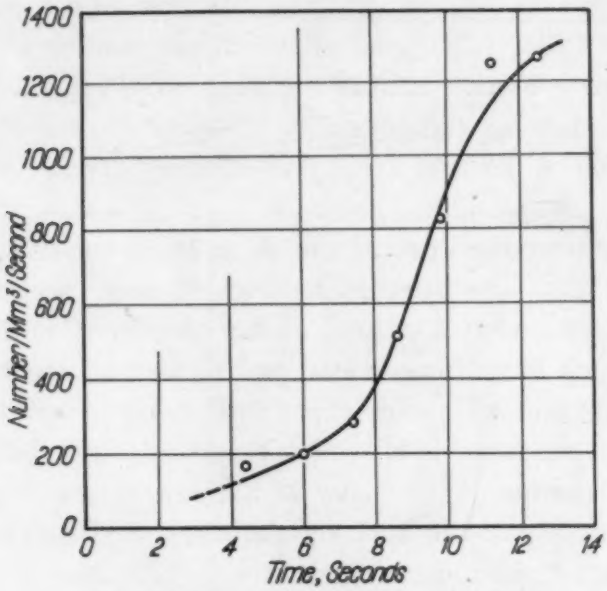

Fig. 26—Rate of Nucleation of Pearlite as a Function of Time. Eutectoid Steel Reacted to Pearlite at 1255 Degrees Fahr. (680 Degrees Cent.).

formation of pearlite at the knee of the S-curve, it is of importance to investigate the circumstances that alter the rate of nucleation at the knee and thus alter the hardenability.

Measurements of the rate of nucleation for the formation of pearlite from homogeneous austenite at high temperatures, near Ae_1, have been made by Hull (20). These show a surprising result, Fig. 26, the rate of nucleation increases with time. Many curves have been obtained similar to this, for a variety of steels, and the behavior thus appears general. The reasons for this behavior are not entirely clear. It may be that the strain engendered by the volume change accompanying the formation of pearlite causes the rate of nucleation to increase as the reaction proceeds, for it is known that nucleation is sensitive to strain. But since we have observed the rate of nucleation to increase in a similar manner during an ordinary recrystallization process, where a strain theory could hardly be invoked, perhaps the reason is a more general and fundamental one.

It is not possible to obtain any information on the variation in the rate of nucleation with time near the knee, for as in the case of the rate of growth, the reaction is too fast to be subjected to such measurements. The data given hereinafter are chiefly calculated average rates of nucleation, with any variation with time ignored;

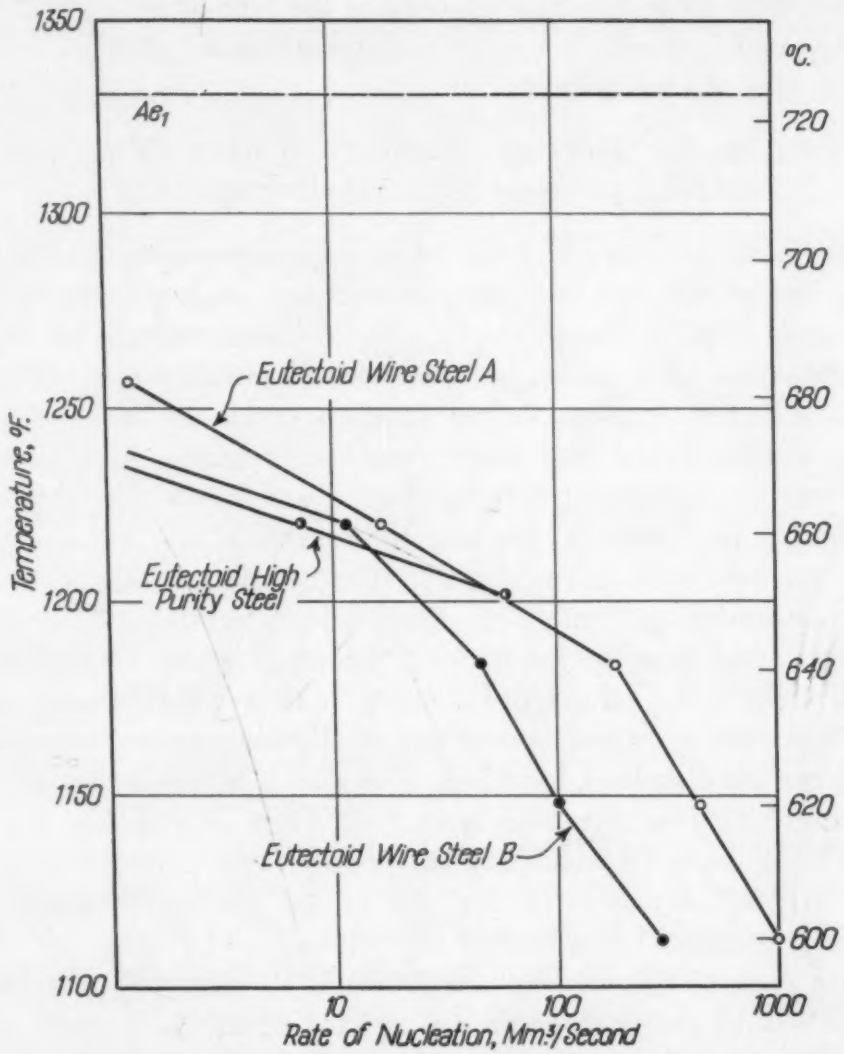

Fig. 27—Rates of Nucleation as a Function of Temperature of Steels as Noted on Curves.

they should serve, nevertheless, to study the influence of the several metallurgical factors, soon to be enumerated, upon the rate of nucleation.

The rate of nucleation increases with decrease in temperature of reaction, as shown in Fig. 27, (20), (28). Curves similar to these are available for a number of steels, including hypo- and

hypereutectoid steels. An increase with falling temperature is to be expected, for simple nucleation theory demands it (22), and it is commonly observed in polyphase reactions. The data plotted near 1060 degrees Fahr. (570 degrees Cent.) are very slightly lower than the true values, owing to the effect of recalescence, as already discussed. Alloy content ordinarily reduces the rate of nucleation, as it does the rate of growth, but again the anomalous cobalt steels exhibit a higher rate of nucleation (30).

Variation in the Rate of Nucleation with Austenitizing Treatment. Grain Size and Heterogeneity

The facts just recited refer to homogeneous austenite. But it seems clear to me that austenite as produced commercially is only infrequently highly homogeneous. The various degrees of departure from this ideal state produce marked variations in rates of formation and in extreme degree produce variations in hardenability. It will be shown that these variations originate in differences in the rate of nucleation; it has already been shown that they cannot originate in differences in the rate of growth.

It has been said that undissolved carbide and undissipated carbon concentration gradients are effective in determining hardenability, that is, the depth of hardening. Bain stated this clearly in the seventh Campbell Lecture (14), citing a case where a steel with residual carbide hardened almost not at all, whereas the same steel, with all carbide dissolved, hardened throughout. Morris and McQuaid at the Hardenability Symposium in 1938 (31), emphasized the necessity for thorough austenitizing to provide homogeneous austenite if full hardenability is to be realized, as did Gordon Williams last year (32), to select but a few of the references.

In a general approach to the problem, Roberts (11) has studied the effect of free carbide on the position of the S-curve, employing the fine- and the coarse-grained steel (17) mentioned previously, Fig. 28. The coarse-grained steel was austenitized 10 minutes at 1345 degrees Fahr. (730 degrees Cent.), furnishing austenite of a grain size of 6½ with residual carbide; the fine-grained steel was austenitized for 30 minutes at 1610 degrees Fahr. (875 degrees Cent.), furnishing an austenite of a grain size of 6 to 6½ without residual carbide. The S-curves determined on sub-critical transformation show clearly that the free carbide moves the S-curve markedly to the left, that is, the rate of transformation

is increased. This effect is generated by an increase in the rate of nucleation brought about by the free carbide. It will be seen on inspecting the figure that the difference between these two S-curves is the lesser the lower the temperature of reaction, and this will later be found to be of importance. It is of some interest also to note

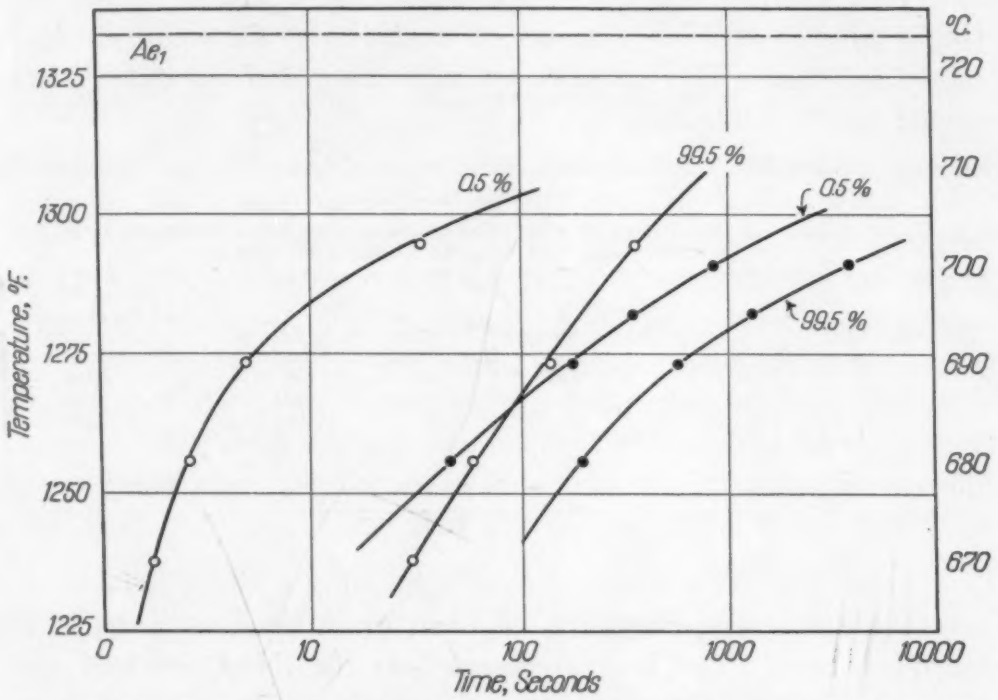

Fig. 28—S-Curves for Reaction from Homogeneous Austenite—Pair of Curves at Right, and from Austenite Containing Undissolved Carbide—Pair of Curves at Left. Eutectoid Steel.

that the slow-reacting steel had been deoxidized with aluminum and thus contained alumina inclusions; in this case, at least, the effect of residual carbide on the rate of formation of pearlite is far greater than any supposed effect of deoxidation products.

In order to embark upon a detailed study of the effect of the degree of homogeneity of austenite upon the rate of nucleation of pearlite, it is necessary to employ a method of comparison of one steel sample to another which will be free from the effect of grain size. Since pearlite nucleates practically exclusively at grain boundaries in homogeneous austenite, the rate of nucleation may be expressed as the number of nuclei formed per second per unit area of the grain boundary surface. From the American Society for Testing Materials grain size, the extent of the grain boundary surface can be calculated; this area per unit volume divided by the

number of nuclei formed per second in the same unit volume, gives the rate of nucleation per unit area of the grain boundary surface. If there are no disturbing factors, if the austenite is truly homogeneous, this rate of nucleation will be a constant irrespective of grain size.

This analysis applied to the isothermal reaction curves at a single temperature for a series of austenite grain sizes, as determined by Bain (33), provides an interesting and somewhat unexpected result, Table II:

Table II

Analysis of Data on the Effect of Austenite Grain Size on Rate of Reaction at 1245 Degrees Fahr. (675 Degrees Cent.) (20), (28)

Austenitized ½ Hour at °F.	Grain Size	Grain-boundary Area Mm.²/Mm.³	Time for Half Reaction Sec.	Rate of Nucleation Per Mm.³	Relative Rates of Nucleation Per Mm.² of Grain-boundary Area
1550	8	107	3.2	$800 \cdot 10^8$	7400
1650	4-8 (6)	54	7	$340 \cdot 10^2$	630
1750	2-6 (4)	27	14	2200	80
1850	2-6 (3)	19	16	1200	66
1950	2-6 (2)	13	18	80	60

These data were obtained by austenitizing a single steel at different temperatures, providing different grain sizes, as listed in the second column. The fourth column lists the times for half reaction and the last column the rates of nucleation per unit area of the grain boundary surface. The rates of nucleation in the last column are relative and not true rates, obtained in the manner suggested earlier, that is, by assuming a value of the rate of growth, and with this and the reaction curve, the rate of nucleation calculated.

The results show that the rate of nucleation per unit grain-boundary area is not a constant, and it is clear therefore that the variations in reaction rate near Ae_1 shown do not arise from grain size alone; on the contrary, the results on samples of small grain size austenitized at low temperatures are in large measure determined by a variation in the rate of nucleation apart from grain size, presumably by undissolved carbide and undissipated carbon concentration gradients.

The effect of time of austenitizing upon the rate of nucleation has been studied, and the results can be interpreted with more certainty, Table III.

The steel was a commercial simple-carbon eutectoid steel with

Table III

Effect of Austenitizing Time at 1610 Degrees Fahr. (875 Degrees Cent.). Upon Rates of Nucleation at 1255 Degrees Fahr. (680 Degrees Cent.) (20)

Time at 1610° F. Min.	Fracture Grain Size	Grain-boundary Area Mm.²/Mm.³	Time for Half Reaction Sec.	Rate of Nucleation Per Mm.³	Rate of Nucleation Per Mm.² of Grain-boundary Area
5	6¼	57	57	62.5	1.1
10	5¼	42	198	0.43	0.01
16	4¾	35	300	0.081	0.0023
30	4¼	29	378	0.057	0.0020
90	3¾	25	420	0.021	0.00084

0.80 per cent carbon, 0.74 per cent manganese, silicon-killed; after austenitizing, it was reacted to pearlite at 1255 degrees Fahr. (680 degrees Cent.). The austenitizing temperature was 1610 degrees Fahr. (875 degrees Cent.), and the times of austenitizing are shown in the first column. The American Society for Testing Materials grain sizes are shown in the second column, and the times of half-reaction rate are given in the fourth column; these times would ordinarily be taken as an example of the effect of grain size on the rate of reaction, but the rates of nucleation, calculated as before to unit grain-boundary area, show that this is not strictly true, for these rates of nucleation, as listed in the last column, are observed to vary by a factor of 1000 between 5 minutes and 90 minutes of austenitizing.

Microscopic study showed carbide present after 5 and 16 minutes of austenitizing, but apparently absent after longer austenitizing. It seems clear that these results arise from the effect of undissolved carbide and probably also from the effect of undissipated carbon concentration gradients.

It must be kept clearly in mind that these rates apply to a temperature near Ae_1. Colton has performed similar studies for a reaction temperature of 1100 degrees Fahr. (595 degrees Cent.), which is close to the knee. These are shown in Table IV.

Table IV

Effect of Time of Austenitizing at 1610 Degrees Fahr. (875 Degrees Cent.) on the Rate of Nucleation at 1100 Degrees Fahr. (595 Degrees Cent.) (28)

Time at 1610° F. Min.	Fracture Grain Size	Grain-boundary Area Mm.²/Mm.³	Time for Half Reaction Sec.	Rate of Nucleation Per Mm.³	Rate of Nucleation Per Mm.² of Grain-boundary Area
5	6¼	58	2.7	2.4×10^4	4.2×10^2
10	5¼	42.5	3.0	1.6×10^4	3.7×10^2
16	5½–5¾	47.5	3.25	1.2×10^4	2.4×10^2
30	4½–5	35	3.50	0.9×10^4	2.5×10^2
90	4 –4½	29	4.0	0.5×10^4	1.8×10^2

We see an important result in this table: differences in austenitizing time still exert a sensible influence upon the rate of reaction and upon the rate of nucleation, but it is very much smaller than that at temperatures near Ae_1—a factor of 2 instead of a factor of 1000.

This behavior suggests that undissolved carbide and undissipated carbon concentration gradients provide a certain number of nuclei for the formation of pearlite which is nearly as effective at a high as at a low temperature, and that this number is very large compared to the small number of normal nuclei formed in unit time near Ae_1, but is relatively small compared to the very large number of normal nuclei formed in unit time near the knee. It will be remembered that the effect of carbide in displacing the S-curve to the left, given in an earlier figure, showed this same result in terms of reaction rates. It is very important indeed to note, then, that we cannot use relative rates of reaction near Ae_1 to predict relative rates near the knee or to predict the correlated hardenability. Evidently, then, the rate of reaction near Ae_1 is far more sensitive to small variations in homogeneity in austenite than the rate near the knee. This fact should be of some importance in the heat-treatment of very large sections, which upon quenching react to pearlite, transforming at relatively high temperatures. It would appear that such sections should be homogenized unusually thoroughly in order to decrease the rate of formation of pearlite, and accordingly upon cooling to react at a lower temperature, giving a finer pearlite and thus a greater ductility and strength. From what has been said it is obvious that ordinary depth of hardening tests would be entirely unreliable in predicting this behavior.

The temperature of reaction of 1100 degrees Fahr. (595 degrees Cent.) in Table IV is a little higher than the temperature at the knee of the S-curve. If the data given were applicable to the reaction precisely at the knee, we might expect some difference, probably small, in hardenability, but simple end-quenching hardenability tests show no detectible difference in hardenability between 5 and 90 minutes of austenitizing; it is possible, of course, that a more sensitive hardenability test might have shown a slight difference. It seems, therefore, that the amount of carbide left undissolved after 5 minutes of austenitizing at 1610 degrees Fahr. (875 degrees Cent.) is inadequate to cause a marked difference in hardenability.

Studies aimed at disclosing the rôle played by austenite heterogeneity on the rate of formation of pearlite may be made by altering

the temperature of austenitizing rather than time of austenitizing as just recounted. For this purpose, a similar steel was employed, for which the temperature of austenitizing was varied between 1470 and 2190 degrees Fahr. (800 and 1200 degrees Cent.) with the time of austenitizing constant at ½ hour. Rates of nucleation per unit grain-boundary area for reaction to pearlite near Ae_1, at 1275 degrees Fahr. (690 degrees Cent.), were found to vary between the austenitizing temperature extremes cited by a factor of as high as 6000. Data obtained for reaction at 1100 degrees Fahr. (595 degrees Cent.), which is near the knee, show the extreme difference in the rates of nucleation now to be reduced to the small factor of 10, a result comparable to that given before for the effect of austenitizing time. The samples austenitized at 1470 degrees Fahr. (800 degrees Cent.) contained undissolved carbide and showed a marked tendency toward general nucleation, whereas those austenitized at the higher temperatures, in which no carbide could be detected, showed purely grain boundary nucleation.

The last observation appears to have some general significance. At the moment it appears that free carbide particles must be reasonably numerous and small to exert an appreciable effect upon hardenability, and it appears also that when such a condition obtains in austenite, pearlite tends to nucleate generally throughout the austenite grain and not solely at the grain boundary. Conversely, if in a hardenability test specimen the partially hardened zone exhibits pearlite nodules distributed generally and not restricted to nor even preferentially located at the austenite grain boundaries, it may be suspected that the steel in this condition is rapidly reacting, and therefore of abnormally low hardenability.

It is interesting that pure steels austenitize much more readily than commercial steels, and upon transformation at the knee show practically pure grain-boundary transformation, whereas commercial steels, austenitizing much more slowly, frequently show general nucleation; Colton (28) has shown clearly that the more thorough the austenitizing treatment in commercial steels the more complete is transformation of the grain boundary type.

Few coarse carbides appear to be relatively ineffective in hardenability, but numerous small carbide particles exert an effect which is pronounced; the annealing sensitivity, about which Gill (34) has written recently, depends upon this. Roberts (11) has been able to show that an annealing treatment intruded between the initial

and final quench in a steel characteristically containing free carbide, coarsens this carbide, rendering it relatively ineffective and thus producing deeper hardening. Luerssen reported upon a case similar to this in the Hardenability Symposium in 1938 (35). Steels with anomalous hardenabilities are frequently reported, but in at least many of these cases the reason does not lie in any mysterious effect of furnace practice, but lies in the unsuspected presence of carbide.

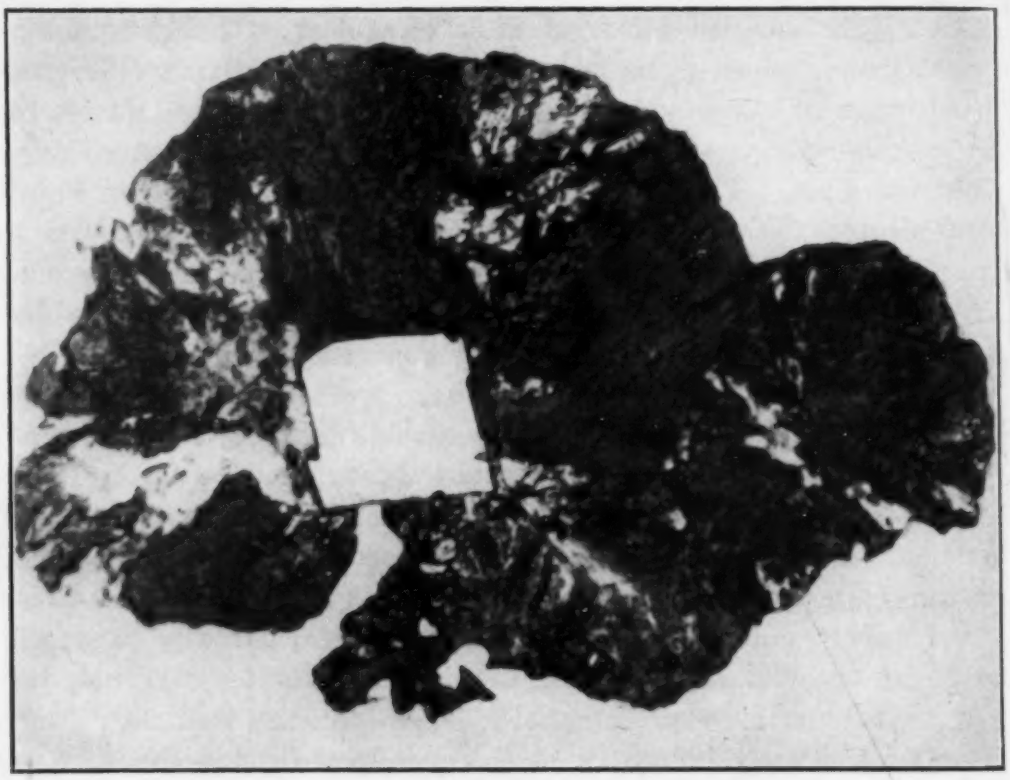

Fig. 29—Pearlite Forming at Inclusion in an Hypereutectoid Steel Partially Reacted at 1180 Degrees Fahr. × 3200.

In attempting divination of such cases, it would appear advisable to look first to the state of homogeneity of austenite.

Effect of Deoxidation Practice. The opinion is held by some that deoxidation practice has an influence upon the rate of formation of pearlite and upon hardenability apart from the effect of deoxidation upon grain size and apart from any effect of residual carbide. A number of such cases were cited at the Hardenability Symposium in 1938, and several others have been cited since in papers before this Society. This opinion appears to rest on two bases, first, that since observers report differences in hardenability

which they have been unable to attribute to differences in grain size or composition, some effect must be present, possibly an unknown effect of deoxidation practice, and second, that since inclusions are sometimes observed to exert a nucleating effect upon pearlite, Fig. 29, variations in deoxidation practice, producing various types of inclusions, ought to produce differences in hardenability.

It is at least clear that a rigid distinction must be drawn between, on the one hand, the effect of deoxidation upon grain size and this in turn upon hardenability, and on the other hand, the effect which deoxidation products has upon hardenability apart from the operation of grain size.

Cash, Merrill, and Stephenson observed in 1939 (17) that when a fine-grained part of a heat, deoxidized with aluminum, was austenitized to give the same grain size as that of a coarse-grained part of the same heat, the depth of hardening was the same, and they drew the conclusion that deoxidation with aluminum affects hardenability only through its effect on grain size.

Hull (20) has determined the rate of nucleation of these two steels at 1255 degrees Fahr. (680 degrees Cent.) after austenitizing to a single grain size at temperatures high enough almost certainly to avoid any effect of carbon heterogeneity. The results are given in Table V.

Table V

Effect of Deoxidation with Aluminum on the Rate of Nucleation at 1255 Degrees Fahr. (680 Degrees Cent.)

Steel	Austenitizing Temperature (½ Hr.) °F.	Grain Size A.S.T.M.	Rate of Nucleation Per Mm.² of Grain-boundary Area
Fine-grained	1875	3	0.016
Coarse-grained	1695	3	0.0044

There is a difference in the rates of nucleation at this temperature, but only by a factor of four. Colton (28) has obtained similar data for rates of nucleation near the knee, at 1100 degrees Fahr. (595 degrees Cent.), and these show a difference, but only by the small factor of two. The difference must be even less, exactly at the knee, and such a difference is inadequate to produce a measurable difference in hardenability. With the austenitizing treatments employed, no residual carbide could be detected, and nucleation was predominantly grain-boundary. It is clear from this that such deoxidation exercises only a minor influence upon the rate of formation of pearlite at all temperatures.

There can be no doubt that deoxidation products can cause nucleation within the grain similar to that caused by residual carbide, as shown by Bain in 1932 (14), as cited by Morris and McQuaid in 1938 (31), by Greene in 1941 (36), by Grossmann and Stephenson in 1941 (23), and others, but the effect is slight, and similar to that caused by small amounts of residual carbide which have been shown to be ineffective in varying hardenability; the effect of such nucleating inclusions in ordinary commercial steels cannot equal in power the effect of large amounts of residual carbide. In each case the small amount of general nucleation produced is but equivalent to a very minor change in grain size. As Burns showed in 1938 (37), variations in residual alloy in commercial steel are ordinarily great enough in their effect upon hardenability much to exceed this relatively minor effect.

Thus far, in summary, it appears to me a fair statement that variations in hardenability are brought about first by variations in grain size, as this is determined by deoxidation practice, affecting the rate of nucleation per unit volume; second, by variations in composition—deliberate or accidental—affecting both the rate of nucleation and the rate of growth; and third, by inadequate carbide solution, affecting the rate of nucleation. There is no case proven as an exception to this of which I am aware, nor does it seem possible that there should be one in ordinary commercial steels.

Conclusion

These, gentlemen, are some observations concerning the rate of formation of pearlite from austenite as it has been possible to gather them thus far, in the quantitative terms of the rate of nucleation and the rate of growth. I hope that you have found the account of some interest.

This subject of the decomposition of austenite is the oldest, yet also still the newest, for metallurgical research. No one could readily believe that the subject is exhausted, and there can be no doubt but that it will continue to interest the investigator for many years to come.

When Roberts-Austen lectured on "The Hardening and Tempering of Steel" in 1889 (38), he expressed his fascination in the subject by quoting a seventeenth century writer, Meric Casaubon: "And if any men think that I make too great a wonder of it, as I

know there be many (never born to be Philosophers) who can hardly be brought to admire anything that is known and ordinary: I could appeal to many both ancient and late, men of great reputation and learning . . . who have given it place among the greatest miracles of the world."

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RAPID TEMPERATURE MEASUREMENTS OF MOLTEN IRON AND STEEL WITH AN IMMERSION THERMOCOUPLE

By Fulton Holtby

Abstract

Accurate temperature measurements of small amounts of molten iron and steel were found to be difficult to obtain using commercial pyrometers.

The construction, calibration, and operation of a new type of tungsten-graphite immersion thermocouple is discussed. The author reports that this thermocouple can obtain temperature readings of molten iron and steel in 10 seconds without causing measurable chemical changes in the metal. This thermocouple has very small e.m.f. values at cold junction temperatures and large e.m.f. values in the range of molten iron and steel.

This tungsten-graphite thermocouple does not cause inoculation or graphite seeding of molten iron as is usually the case when graphite protected platinum-platinum 10 per cent rhodium immersion thermocouples are used for temperature measurements.

Introduction

RESEARCH investigations which are being carried on at the University of Minnesota foundry laboratory require a large number of quick, accurate, and relatively high temperature measurements of molten iron and steel. Several commercial pyrometers were used in trying to obtain these readings, but without success. This paper will discuss the construction and operation of a thermocouple developed to obtain the desired results.

Temperature Requirements

The temperature measuring device used in these investigations had to satisfy the following requirements:

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A. Rapid, accurate measurements of molten cast iron at 2800 degrees Fahr. (1540 degrees Cent.) in a small 30-pound hand ladle.

B. Measurements of 30- to 150-pound ladles of molten iron and steel without any change in the chemical analysis or physical properties of the metal.

Commercial Pyrometers Did Not Meet Research Requirements

In our research investigations certain materials added to the molten cast iron caused excessive fumes and slag in the furnace and in the ladles. Temperature readings with two different types of optical pyrometers, under these conditions, gave variable readings of 250 to 350 degrees Fahr. (120 to 175 degrees Cent.) lower than the actual temperature as shown by a calibrated platinum-platinum 10 per cent rhodium thermocouple.

A platinum thermocouple, when used to measure temperatures of molten cast iron, must have two protecting tubes. The inner tube must be gas-tight to protect the platinum wires from carburizing gases. The outer tube must protect the inner tube from rapid thermal shock and from corrosive slag or gases. Most commercial platinum thermocouples use sillimanite for the inner tube and graphite for the outer tube. Various sizes and combinations of these protecting tubes were tried with a platinum thermocouple, but, because of their thermal lag, none would allow a reading to be made in less than 1.5 minutes.

The Tungsten-Graphite Thermocouple

The errors in the optical pyrometer readings due to smoke and slag conditions, and the temperature limitations and thermal lag of the protected noble-metal couple, made it necessary to build special pyrometers for these research investigations.

A tungsten-graphite thermocouple as shown in Figs. 1 and 2 was built and used for several months. The construction, calibration, and operation of this thermocouple are described in a previous paper[1] by the author. This pyrometer had the following advantageous features:

[1] F. Holtby, "Rapid Temperature Measurements of Cast Iron with an Immersion Thermocouple", *Transactions*, American Foundrymen's Association, Vol. 47, 1939, p. 854.

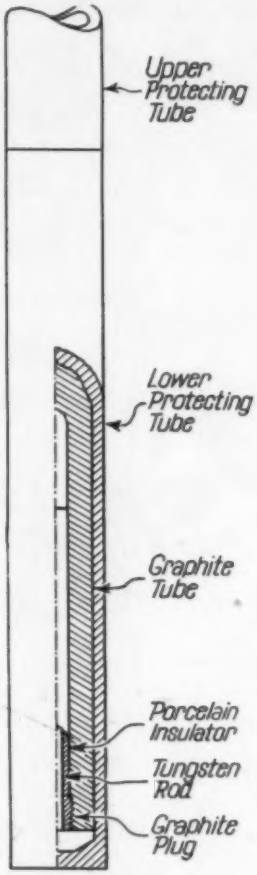

Fig. 1—Tungsten-Graphite Thermocouple Hot Junction End and Protecting Tubes. (Old Model).

A. Temperature measurements could be made up to at least 3300 degrees Fahr. (1815 degrees Cent.).

B. Temperature readings in small ladles of iron could be made in less than 70 seconds.

C. Temperature measurements were unaffected by the presence of smoke or slag.

D. The thermal e.m.f. was higher than that of any other commercial thermocouple having a negligible cold junction correction.

This tungsten-graphite thermocouple, after being used for several months, showed two serious disadvantages. First, the thermocouple could not obtain temperature readings from small ladles of molten steel before loss of fluidity resulted, and second, the graphite protecting tube used with this couple caused inoculation of the cast iron.

A Revised Form of the Tungsten-Graphite Thermocouple

A new form of the tungsten-graphite thermocouple was developed to eliminate these two disadvantages. This instrument, when used in connection with a potentiometer or a millivoltmeter, is used to measure the temperature of molten cast iron or molten steel. It is believed that this instrument measures the temperature of molten

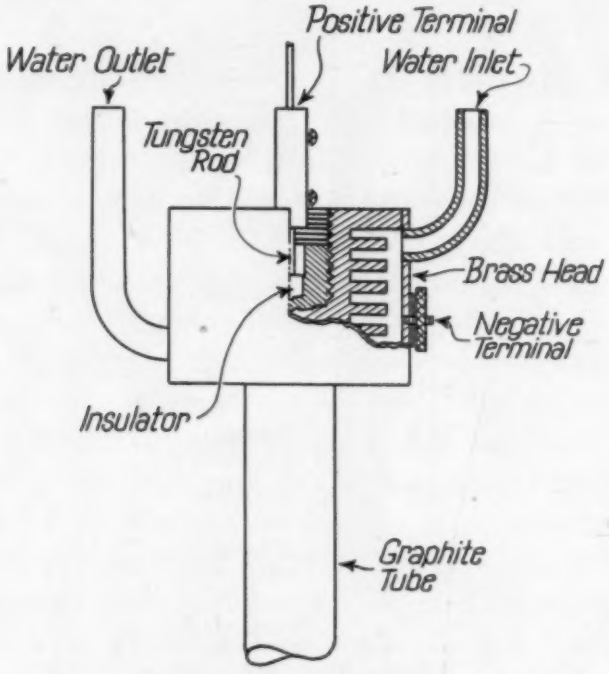

Fig. 2—Tungsten-Graphite Thermocouple Cold Junction Head and Terminals. (Old Model).

iron and steel faster and more accurately than any other instrument now on the commercial market.

The instrument, shown in Figs. 3, 4, and 5, is composed of an electrical circuit, an asbestos housing, a shield, a handle, and a combination clamp and cold junction compensator.

The positive half of the electrical circuit is made up of a length of fourteen or eighteen gage tungsten wire, a copper pressure plate on the compensator, and a copper wire leading from this plate to the fixed cold junction in the handle. The negative half of the electrical circuit consists of a $\frac{5}{16}$-inch diameter spectroscopic graphite rod, a phosphorus-bronze wire leading from the plate to the fixed junction in the handle. The plates bear tightly against the rods, and the compensating wires are silver soldered to the plates to provide good electrical connection. These wires are attached to standard

copper wires, to form the fixed cold junction in the handle, by incasing the wire ends in short lengths of copper tubing, sealing with solder, and insulating with rubber tubing and rubber tape.

The housing is made of ½-inch asbestos board, and consists of a base and a cover. The base is equipped with screw holes for fastening the shield, the handle, and the compensator; grooves to hold the wires leading from the compensator to the fixed cold

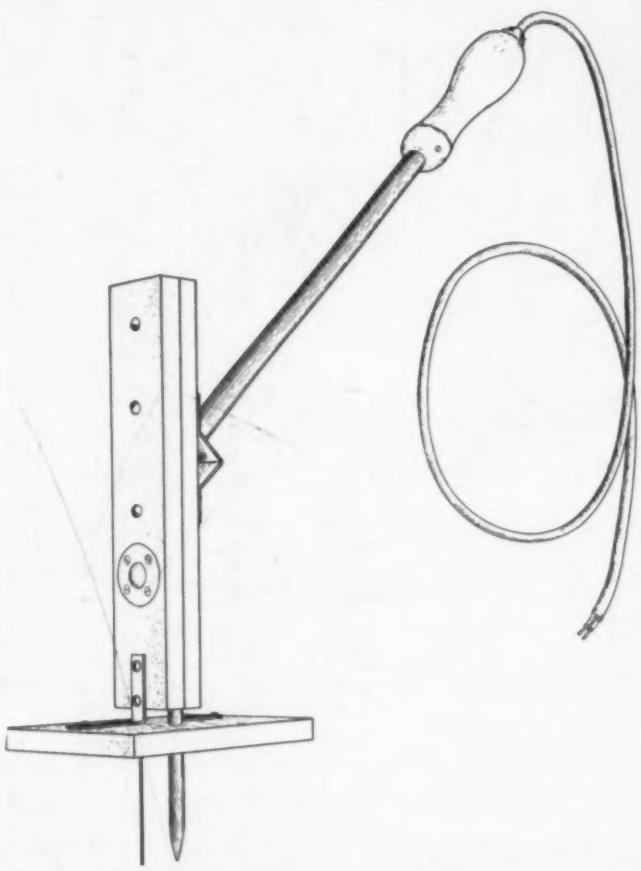

Fig. 3—Tungsten-Graphite Thermocouple. (New Model).

junction; and a semi-cylindrical groove to form a seat for the graphite rod. The cover has a groove and screw holes to match the base, but also has a groove for the tungsten rod and a hole into which the compensator fits.

The shield consists of a square of asbestos board and two steel brackets, which fasten it to the housing. Holes ⅜ inch in diameter are drilled in the proper places to allow the tungsten and graphite rods to extend out beyond the shield. The purpose of the shield is to

prevent the transmission of excess radiant heat from the molten metal to the instrument.

The handle is made up of a brass tube and a standard wooden grip. The tube is fastened to the base, a little behind center and at an angle of 45 degrees, by means of a formed steel bracket to

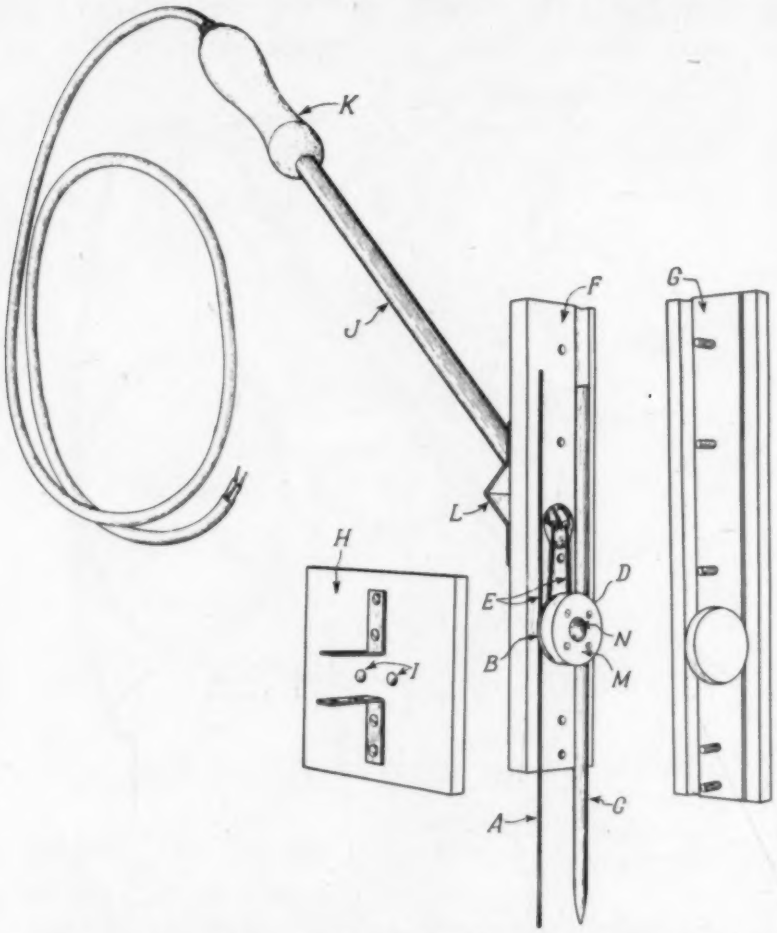

Fig. 4—List of Parts of Tungsten-Graphite Thermocouple. A. Tungsten Rod; B. Copper Pressure Plate Against Tungsten Rod; C. Graphite Rod; D. Phosphorus-Bronze Pressure Plate Against Graphite Rod; E. Compensating Wires; F. Housing Base; G. Housing Cover; H. Protecting Shield; I. Holes for Rods; J. Handle Tube; K. Handle Grip, Containing Fixed Cold Junction; L. Formed Bracket; M. Combination Clamp and Compensator; N. Carriage Bolt.

which it is brazed, and also by extending the tube into a hole in the housing base. The hollow tube contains the wires leading from the compensator to the fixed cold junction. The grip is of standard construction and is fastened to the arm by means of a machine screw. It is hollow and contains the connection which was described as the fixed cold junction of the electrical circuit.

The combination clamp and cold junction compensator is made

up of two pressure plates fastened to a circular piece of asbestos board. These plates are arranged in step-fashion, so that they bear firmly against both the thick graphite rod and the thin tungsten wire when the compensator is tightened in place. The compensator is held to the housing base by means of a carriage bolt and a wing nut. The bolt is screwed into the asbestos disk and sealed in with water glass.

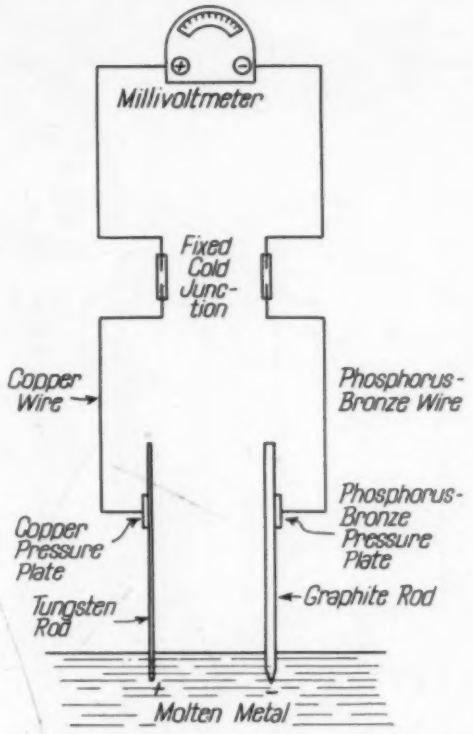

Fig. 5—Wiring Diagram of Tungsten-Graphite Thermocouple.

Screwed into the compensator is a small fillister-head machine screw, with the head protruding. This head, fitting into a hole in the base, determines how the compensator is placed in relation to the base. This prevents the switching of the copper and phosphorus-bronze plates besides centering the compensating wires in their grooves. The functions of the compensator are to hold the graphite and tungsten elements in place, and also to provide electrical connections which will not introduce additional electromotive forces into the circuit. The combination of tungsten against copper and graphite against phosphorus-bronze allows the instrument housing and compensator to be heated up to 300 degrees Fahr. (150 degrees Cent.) with the algebraic sum of the electromotive forces generated at these junctions remaining equal to zero.

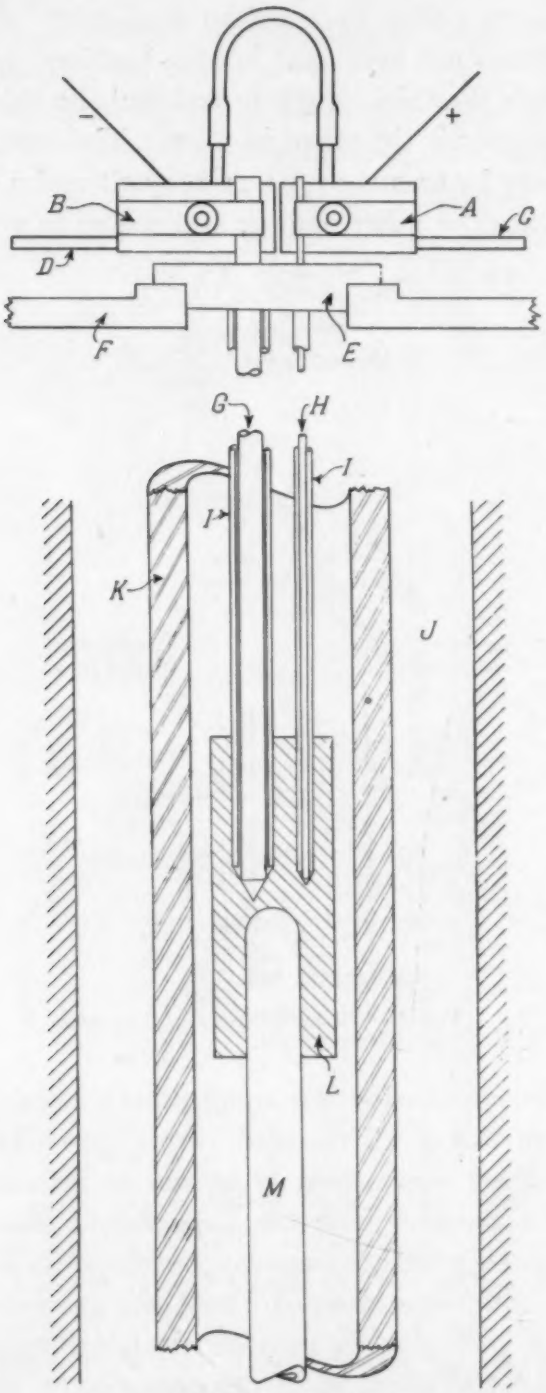

Fig. 6—Method of Calibrating Tungsten-Graphite Elements Using Graphite Block. A. Positive Terminal; B. Negative Terminal; C. Water Inlet; D. Water Outlet; E. Asbestos Cover; F. Furnace; G. Graphite Element; H. Tungsten Element; I. Sillimanite Tubes; J. Furnace Wall; K. Globar Heating Element; L. Graphite Block; M. Platinum-Platinum 10 Per Cent Rhodium Thermocouple.

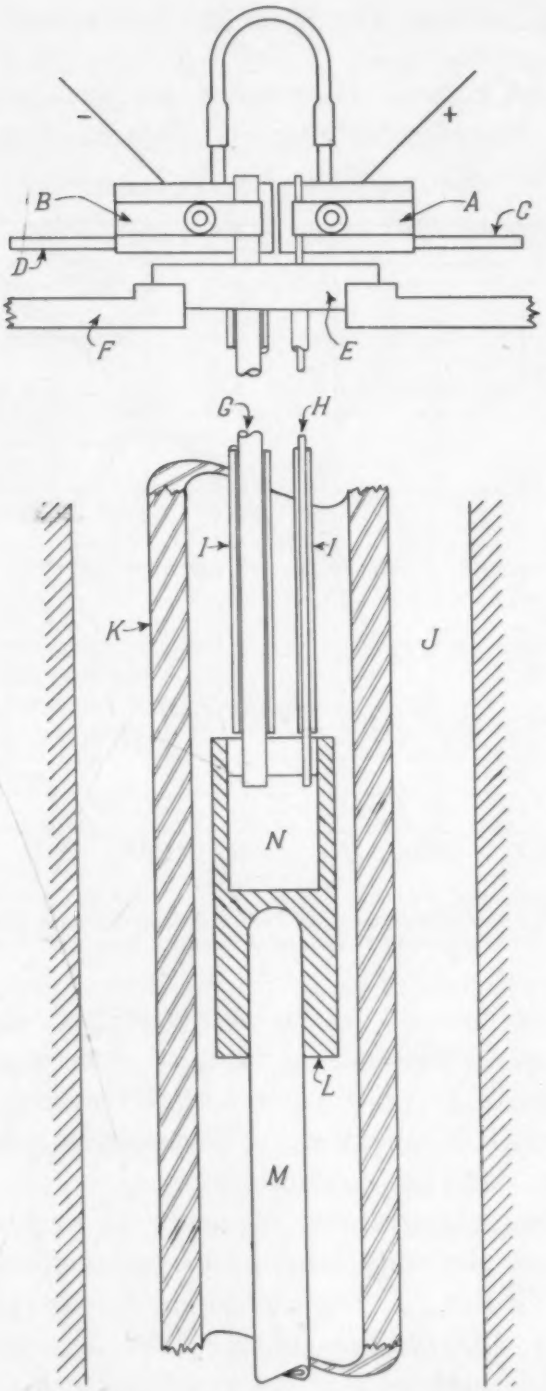

Fig. 7—Method of Calibrating Tungsten-Graphite Elements Using Molten Iron. A. Positive Terminal; B. Negative Terminal; C. Water Inlet; D. Water Outlet; E. Asbestos Cover; F. Furnace; G. Graphite Element; H. Tungsten Element; I. Sillimanite Tubes; J. Furnace Wall; K. Globar Heating Element; L. Graphite Block; M. Platinum-Platinum 10 Per Cent Rhodium Thermocouple; N. Molten Iron.

The Calibration of the Tungsten-Graphite Elements

The tungsten element is either a fourteen or eighteen gage, swaged, caustic-cleaned tungsten wire. It is not heat treated in any way before calibration.

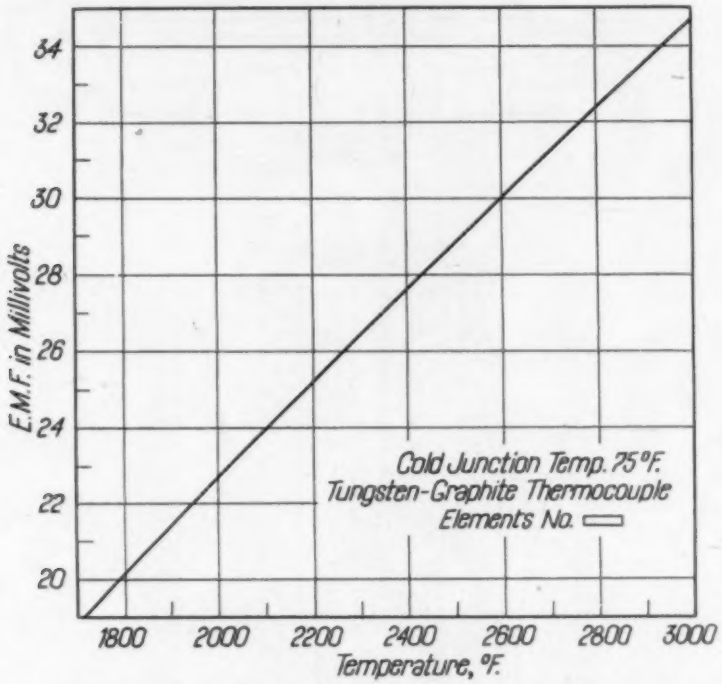

Fig. 8—Calibration Curve of Tungsten-Graphite Thermocouple for Temperature Ranges of Molten Iron and Steel.

The graphite element, which is a standard $\frac{5}{16}$-inch diameter spectroscopic graphite electrode, is annealed at between 3300 to 3600 degrees Fahr. (1815 to 1970 degrees Cent.) in an induction or an arc furnace, before it is calibrated. This annealing process eliminates any change in the rod after calibration.

The tungsten and graphite elements are calibrated in pairs against a standard platinum-platinum 10 per cent rhodium thermocouple as shown in Fig. 6. The calibration furnace is brought up to a temperature of 2200 degrees Fahr. (1205 degrees Cent.) and a pair of elements is inserted into the graphite block in the center of the furnace. The temperature of this block is read from the platinum-platinum 10 per cent rhodium thermocouple circuit and the equivalent e.m.f. value of the tungsten-graphite elements recorded. A graphite crucible of molten iron may be used in place of the graphite block as shown in Fig. 7. This calibration is repeated at 2400, 2600 and

2800 degrees Fahr. (1315, 1425 and 1540 degrees Cent.). These e.m.f. values, when corrected for cold junction values, give a curve similar to that shown in Fig. 8. This calibration curve is then used with its corresponding pair of elements when temperature readings are made with the tungsten-graphite thermocouple.

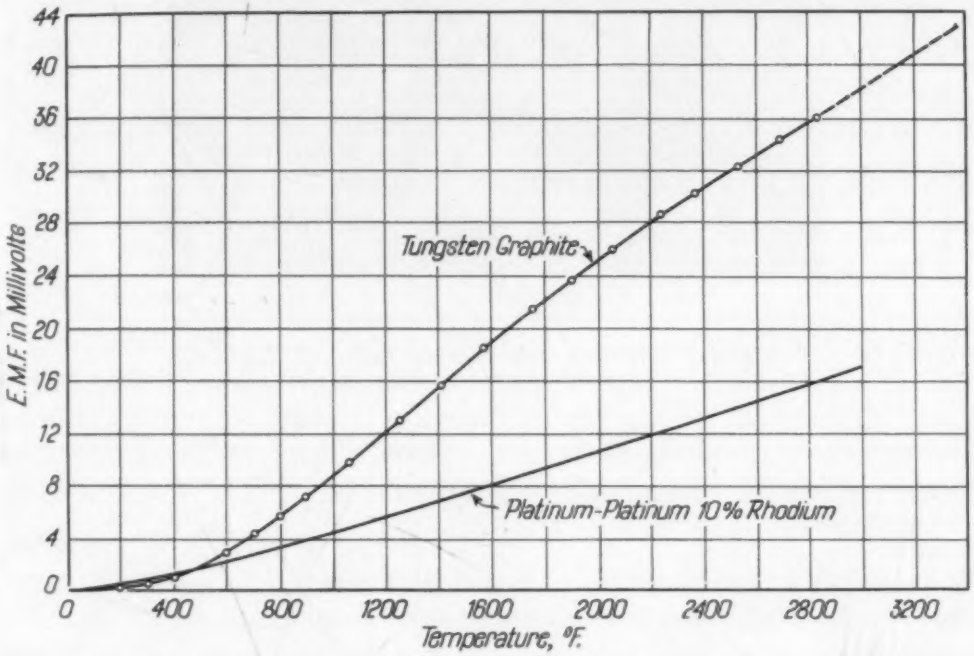

Fig. 9—Calibration Curve of Tungsten-Graphite Thermocouple as Compared to Platinum-Platinum 10 Per Cent Rhodium Thermocouple.

A complete temperature millivolt calibration curve for a pair of tungsten-graphite elements is shown in Fig. 9. This curve shows that tungsten-graphite thermocouples have very small e.m.f. values up to 300 degrees Fahr. (150 degrees Cent.) and large e.m.f. values in the temperature range of molten iron and steel. This is very desirable when measuring the temperature of these molten materials since a change of 10 to 20 degrees Fahr. in the cold junction does not greatly affect the temperature reading.

The Operation of the Tungsten-Graphite Thermocouple

The operation of this instrument consists of touching the molten metal, either iron, steel, or any other metallic substance, with the tungsten and graphite elements, and obtaining the equivalent millivolt reading at the potentiometer or millivoltmeter. The temperature of the molten metal connecting the tungsten and graphite rods can be

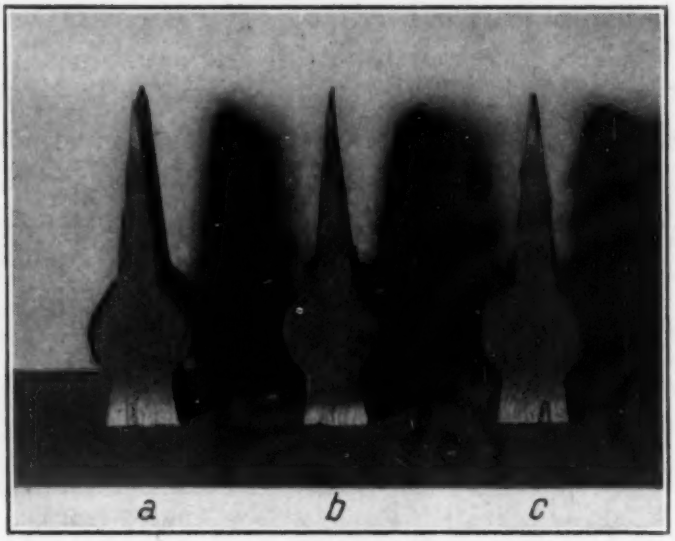

Fig. 10—Chill Test Bars Showing Effects of Inoculation from Graphite Tube Protected Immersion Thermocouple.

observed on the calibration curve, which shows millivolt readings plotted against the corresponding temperatures.

As the tungsten or graphite elements are burned or oxidized away, they are moved forward in the instrument by lifting the compensator, moving the rods forward, and then again tightening the compensator.

A millivoltmeter, having a scale range of 0 to 50 m.v., resistance of 500 to 1000 ohms, and an accuracy of ½ per cent of full scale reading, is recommended for use with this thermocouple. Any type of potentiometer can be used, providing it has the necessary capacity; but a potentiometer is usually slower in operation than a millivoltmeter.

Advantages of the Tunsten-Graphite Thermocouple

The temperature millivolt readings of molten iron or steel can be obtained in from 7 to 10 seconds, and are so rapidly obtained that inoculation of the molten metal, or a change in chemical analysis, is negligible. When slag is present on the surface of the molten metal, the two elements can be pushed through the slag and the reading obtained when the two elements come in contact with the molten metal. Readings up to as high as 3600 degrees Fahr. (1970 degrees Cent.) have been made with this instrument. Readings

have even been made in 10-pound batches of molten steel with no change in chemical analysis.

Fig. 10 shows what may happen in test work from inoculation of the metal from a thermocouple. All three chill test bars were from the same furnace tap and were held in separate hand ladles for the same length of time. A was poured with the metal having no temperature readings taken. B was poured with the metal after a temperature reading was obtained in 60 seconds, using a commercial graphite protected thermocouple. C was poured with the metal after the temperature reading was obtained in 8 seconds with the revised form of the tungsten-graphite thermocouple.

DISCUSSION

Written Discussion: By A. E. Schuh, director of research, United States Pipe and Foundry Co., Burlington, N. J.

Mr. Holtby has made a real contribution towards facilitating the reliable temperature measurement of molten iron or steel in the laboratory. The thermocouple employed responds very rapidly and during the short immersion periods used, the amount of dissolution of the thermal-elements, owing to their small size, is sufficiently small to avoid trouble due to contamination of the melt. In a limited trial of this instrument at our laboratory it was found that if the instrument is immersed more than fifteen seconds, the tungsten-element begins to go into solution. The short immersion time dictates the use of a rapidly responding millivoltmeter instead of the customary potentiometer; however, due to the high e.m.f. generated by the couple the use of a millivoltmeter appears entirely feasible. Owing to the shallow depth of immersion, and to the short time of exposure, the consumption of the electrodes is economical.

The instrument, due to its lightness and the fragility of the electrodes, is not suitable for normal shop purposes. There is still a real need for an instrument for this purpose. Optical pyrometers, although fast, are not altogether dependable due to the presence of fumes, surface compounds having variable emissivity, and the human equation. Most portable immersion instruments are too sluggish in their response to make possible the quick reliable readings which are frequently necessary in any shop. Reduction of mass, in order to accelerate response, is usually accompanied by an excessive loss of ruggedness.

Written Discussion: By L. F. Miller, professor of physics, University of Minnesota, Minneapolis.

Sometimes the demand for some special form of instrument is so extensive in some one field that it is worth while to develop a particular type even though its application may be quite restricted. This seems to be quite the case with this special form of graphite-tungsten pyrometer devised by Professor Holtby. The particular application here is in the foundry where limited melts of iron and steel are being handled. The molten medium, the temperature of which is being measured, must be conducting. This device cannot be applied then to

nonmetallic melts. There are numerous other metallic melts i.e., tin, lead, zinc, aluminum, etc., but the best working range for this graphite-tungsten combination is over 2000 degrees Fahr. (1095 degrees Cent.). There are plenty of other thermocouples available for these lower ranges. The problem involved in obtaining the right quality of graphite or tungsten is practically the same as in selecting materials for other thermocouples. For example, if the right raw materials are selected and properly processed it seems possible to obtain elements having a uniform voltage characteristic and a fairly permanent calibration. There is little difficulty with tungsten as a replaceable in the calibrated thermocouple. As far as the graphite is concerned it is still necessary to frequently do a certain amount of calibrating. However, the possibility of permanent characteristics of a graphite electrode does not seem to be so far away.

It is seen that there is a third element brought into the thermoelectric circuit by having the graphite-tungsten terminals dipped into the molten medium in order to complete the circuit. This does not disturb the graphite-tungsten thermoelectric relation as long as each of the junctions of the graphite and the tungsten with this third medium are at the same temperature.

Professor Holtby should be commended on the long patient research made to develop his compensating leads. There does not seem to be any mathematical or theoretical method of deriving the right elements. With a few suggestions as a starting point the larger part of the remaining development has been a cut and try method.

The limited quantities of molten metal handled in foundry research tests also raises the question of carbon inoculation since a small amount of carbon injected can become a larger per cent contamination than would be the case in larger melts. Not only does the quick measuring of temperature reduce the danger of this contamination but also the time in which the temperature change can take place is likewise decreased. As a matter of fact the temperature can be so quickly observed that inoculation practically has not time to get started. This may prevent certain defects that often enter when passing from the results obtained with the small test samples to the larger commercial tonnage. The quality and processing of the graphite are also a factor in the extent of inoculation.

Written Discussion: By C. E. Wood, Blast Furnace Studies Section, Metallurgical Division, Bureau of Mines, Minneapolis.

Professor Holtby is to be congratulated upon the development of the rapid-reading tungsten-graphite thermocouple described in this paper. For ascertaining the temperature of small amounts of cast iron and steel the new design appears to be a great improvement over the older tungsten-graphite couples or the platinum-platinum rhodium couple.

A thermocouple of the design shown in Figs. 1 and 2 was first used at the Bureau of Mines Minneapolis station in 1930. Such a device has been employed on a number of occasions since that time in the study of high-temperature reactions under conditions that did not permit use of a platinum couple. An inherent factor that limited the application of this couple was that the thermal e.m.f. of the graphite element changed with continued use. The reason advanced for this change was that the carbon in the element had not been

completely graphitized. Prolonged heating above 3272 degrees Fahr. (1800 degrees Cent.) to effect complete graphitization of the large rods was not very satisfactory with the equipment on hand. It was considered essential that the couple should be calibrated frequently.

This disadvantage apparently has been eliminated by the use of smaller graphite elements with improved properties, and calibration of each graphite element separately is sufficient for the life of that element. The development of a method of making graphite elements with a uniform thermal e.m.f. offers an interesting problem for further research.

Written Discussion: By Karl Fetters, assistant professor of metallurgy, Carnegie Institute of Technology, Pittsburgh.

Professor Holtby has described an ingeneous method of obtaining thermoelectric temperature measurements of molten iron and one that appears to be of considerable value for laboratory studies.

In equilibrium studies of slag metal reactions, however, the presence of a graphite electrode even for a short time would result in undesirable contamination of a highly oxidized bath of molten iron containing perhaps less than 0.005 per cent carbon. Chipman and Fetters[2] have found the use of protected tungsten molybdenum couples to be satisfactory for this purpose and indeed by this time their characteristics have been so well established that they are in regular use in further slag metal studies, and their indications may be accepted with confidence.

Careful annealing of these couples was found to be necessary for consistency of indications when the couples are to be exposed to steel making temperatures for an appreciable length of time since the thermoelectric force of the couple is changed somewhat by recrystallization which occurs. Annealing at a higher temperature than that at which the couple is to be used eliminates this effect. A question might be in order as to whether Professor Holtby observed any changes in e.m.f. after successive exposures of his tungsten element to high temperatures.

It is probable that this recrystallization effect would be minimized by Professor Holtby's technique as it can also be minimized in the tungsten-molybdenum couple by renewal of the bead after short time exposure to high temperature.

Protection tubes of fused silica and of sintered magnesia were used by Chipman and Fetters with satisfactory results. The silica tubes in particular are attacked very little by the metal but considerably by basic slags. This is not too serious for laboratory measurements, but for temperature measurements in the open hearth furnace it imposes a serious obstacle.

Fig. 1A shows typical calibration of annealed tungsten molybdenum couples made from one particular batch of wire. Other batches of wire usually show some differences though not very great. In the temperature range from 2730 to 3090 degrees Fahr. (1500 to 1700 degrees Cent.) this curve may be represented by the parabolic equation:

$$\text{e.m.f. (millivolts)} = 3.872 \times 10^{-6}\ T^2 - 5.444 \times 10^{-3}\ T + 0.589$$

where T is expressed in degrees Cent.

[2] J. Chipman and K. Fetters, "The Solubility of Iron Oxide in Liquid Iron," American Society for Metals, preprint, 1941, No. 54.

It is suggested therefore that an arrangement as shown in Fig. 2A would be sufficiently rugged for temperature measurements in larger furnaces. Here an outer tube is used of the Collins or Sardahl[3] type whereby molten metal or slag is prevented from entering the tip of a steel tube by means of air pressure.

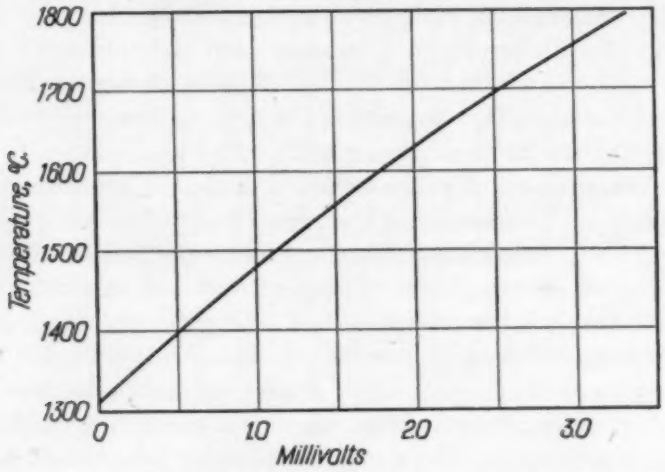

Fig. 1A—Typical Calibration Curve of Tungsten-Molybdenum Thermocouples (Annealed).

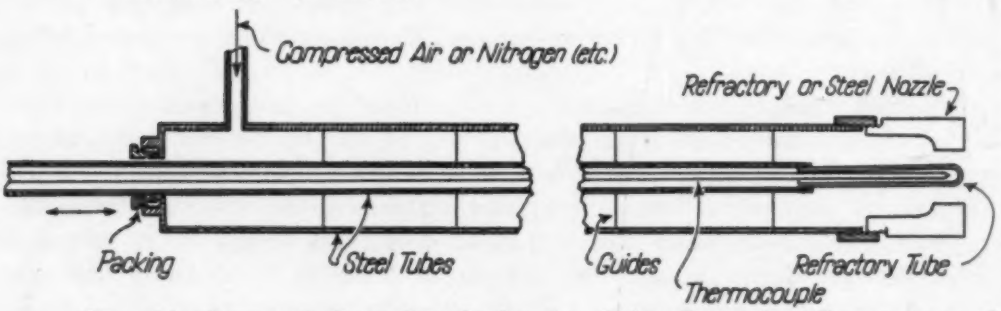

Fig. 2A—Suggested Protection Device for Quick Immersion Temperatures of Molten Steel.

An inner tube would be located in this outer tube in such a manner that after the end of the outer tube had been immersed below the depth of the slag, the inner tube holding the thermocouple and its refractory protection tube could be extended into the molten metal. Then after the thermocouple indication has been obtained, preferably by a high speed recording potentiometer, the couple and its protection tube may be withdrawn into the outer tube and the device removed from the furnace. This device represents a modification of one described by Schofield,[4] but which was found to be unsatisfactory because it involved curved tubes which would of course not telescope readily.

It would be anticipated that this device would give good temperature measurements at a minimum of cost and that its accuracy would not be greatly affected by the air stream in a large bath of metal. A slight modification of this method would be suitable for ladle temperatures, whereas for temperatures of molten metal in molds or in runners no special precautions would be necessary to protect the silica or other refractory tube from slag.

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[3]Collins et al. Patent No. 2,020,092—Sardahl Patent No. 2,184,169.

[4]F. H. Schofield, The Iron and Steel Institute Special Report No. 16, p. 222-238.

Platinum-platinum rhodium or other suitable couples could be substituted for the tungsten-molybdenum couples if desired.

Oral Discussion

G. F. COMSTOCK:[5] I might say that we have used a tungsten-graphite thermocouple that Professor Holtby was kind enough to let us try and we have found it very successful for steel temperatures, using it in an induction furnace where we had previously relied on an optical pyrometer. We sharpened the graphite element to a fine point, and preheated it, and by having one man carefully touch the surface of the bath with the thermocouple elements, and another man reading the potentiometer, we were able to secure readings in ten seconds without any measurable contamination of the molten steel by either carbon or tungsten. Readings obtained in this way ranged from about 2850 to 3100 degrees Fahr. (1565 to 1705 degrees Cent.). This method is very much better than using an optical pyrometer, especially for steels treated with aluminum or titanium, which affect the emissivity of the surface of the molten steel, so that the proper correction to apply to optical readings becomes very doubtful.

Author's Reply

I will first answer Professor Fetter's question as to whether I have observed any changes in e.m.f. after successive exposures of the tungsten elements to high temperatures.

You will notice that in this couple we expect to waste some of the elements. We only expect to obtain 200 to 250 readings from the set of elements before six inches of the original twelve inches is used up. When the elements become too short to hold in the clamping devise we throw them away. We have not found a change in e.m.f. values if we use the elements in this way.

We find that most of the wearing away of these elements is not entirely due to dissolving in the metal but more from oxidation as we remove the couple from the molten metal. To eliminate some of this oxidation we have at times plunged the hot elements, after we take them from the metal, into a can of pulverized refractory material or even just graphite powder.

Since the tungsten rod is gradually used up, the problem of crystallization of the tungsten is eliminated in this type of couple. We have noticed some crystallization of the tungsten element in the couple shown in Fig. 1 after 500 hours of operation at 2800 degrees Fahr. (1540 degrees Cent.) but no change in e.m.f. values.

I might add to this discussion that the graphite companies are very much interested in our results because, from our calibration of a large number of graphite elements, we have shown that there is a possibility of making a little better graphite rod. One graphite company has given us fine co-operation and is now able to supply graphite rods which, in nearly all cases, give us a standard calibration curve. Incidentally, if you contemplate using a thermocouple like this one, do not buy the expensive special spectroscopic graphite

[5]Metallurgist, The Titanium Alloy Manufacturing Co., Niagara Falls, N. Y.

rods. We have found that, for thermocouple work, they are not as good as the standard spectroscopic graphite rods and they cost about 20 times as much. I would suggest that, when buying graphite rods, you ask for rods that are completely graphitized. We are now obtaining rods that do not require any annealing, as described in this paper, before or after calibration.

This instrument is a development after about four years of experimentation in temperature measurements. We have tried a large number of different types of pyrometers and for our research work we believe this couple to fit our needs best. Our problem is to get fast and accurate temperature measurements of small ladles of molten metal. We believe our temperature measurements are now dependable.

I do not recommend this couple for industrial use. It is fragile and cannot be dropped on the floor. However we have four of these units in operation at the University of Minnesota foundry and have very little trouble from breakage even with students using them.

I wish to thank the men for their discussions and assistance. Dr. Schuh has given me fine co-operation by trying this thermocouple in his laboratory. Professor Miller was my professor in a class in pyrometry and from his teachings I was able to develop this unit. Mr. Wood gave me the original idea of using a tungsten-graphite thermocouple and has kindly assisted me in the annealing and calibration problems. Mr. Comstock has tested this unit in an induction furnace and his original reports spurred us to further development. Professor Fetter in his discussion and Fig. 2A has given us a very good idea for temperature measurements. Again I wish to thank these men for their discussions.

THE ALLOYS OF MANGANESE AND COPPER

Microstructure of the Alloys

By R. S. Dean, C. Travis Anderson and J. H. Jacobs

Abstract

Microstructures of Cu-Mn alloys containing 12.5-98 per cent manganese were studied after heating for several hours at various temperatures below the solidus and quenching and after furnace cooling. The most suitable etching agent was determined for each case. Alloys containing 45-80 per cent manganese have a distinctive microstructure, a kind of block structure, possibly due to preferential development of a crystal face common to both lattices. Saturated gamma solid solutions of copper in manganese and saturated solutions of manganese in copper apparently are not isomorphous and this structure may be a type of eutectic. Results showed no evidence that alpha manganese ever separates below 70 per cent manganese. Below 42 per cent manganese, solid solutions of manganese in copper appear stable at ordinary temperatures.

Between 42 and 92 per cent manganese the slowly cooled alloys have a single phase showing no twinning or intergrowth. Copper, up to 2 per cent, forms a solid solution in alpha manganese. Alloys of 42-68 per cent manganese reheated to 500-700 degrees Cent. show a sort of Widmanstätten structure. Above 700 degrees Cent. the structure of quenched alloys reappears. From 70-98 per cent manganese alpha-manganese separates out but redissolves on heating to 600 degrees Cent. Above 750 degrees Cent. alloys containing more than 68 per cent manganese pass either into gamma solid solution or into the gamma plus beta field. The latter have a characteristic microstructure. Veining begins to appear in the gamma solid solution.

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IN the previous articles of this series[1] we have described the electrical resistance, hardening characteristics and vibration damping capacity of the manganese-copper alloys. The present paper deals with the microstructure of the wrought and heat treated alloys.

Preparation and Treatment of the Alloys

All of the alloys were prepared by melting electrolytic manganese and electrolytic copper in an alundum crucible in a 3 k. v. a. high frequency induction furnace. Experience has indicated that with the rapid melting which takes place in this furnace and with the small exposed surface of the bath no deoxidation is necessary to produce sound gas-free ingots. The cast alloys were worked down to ¼-inch rods by swaging. The rods were heated for 2 hours in an atmosphere of helium at a temperature near the solidus and quenched in water. They were examined in this condition and after reheating in vacuo for 2-hour periods at temperatures of 350, 400, 450, 500, 600, 700 and 800 degrees Cent. (660, 750, 840, 930, 1110, 1290 and 1470 degrees Fahr.). After each treatment the alloys were quenched in water. This treatment was chosen because it appeared to bring the alloys more nearly into a state of equilibrium at the various temperatures than any other treatment which would not have required a prohibitively large number of samples. The alloys were also examined in the furnace cooled condition and a number of studies made of alloys reheated after slow cooling. It was found, however, that slowly cooled alloys responded much less readily to reheating than the quenched alloys. At temperatures of 700 degrees Cent. (1290 degrees Fahr.) and above, the same microstructure is obtained by reheating either the quenched or slowly cooled alloys. At lower temperatures, however, the transition in the slowly cooled alloys lagged behind those in the quenched alloys. It may be argued that there is a considerable lag in the transition taking place in the quenched alloys and that the 2-hour period is not sufficiently long to bring about equilibrium. The experiments with somewhat longer heating time have indicated that there is no appreciable change in

[1] R. S. Dean and C. Travis Anderson, "The Alloys of Manganese and Copper: Electrical Resistance," Transactions, American Society for Metals, Vol. 29, 1941, p. 788. R. S. Dean and C. Travis Anderson, "The Alloys of Manganese and Copper: Hardening by Cold Work and Heat Treatment," Transactions, American Society for Metals, Vol. 29, 1941, p. 802. R. S. Dean, C. Travis Anderson and E. V. Potter, "The Alloys of Manganese and Copper: Vibration-Damping Capacity," Transactions, American Society for Metals, Vol. 29, 1941, p. 402.

microstructure after 2 hours heating of the quenched alloys at temperatures above 400 degrees Cent. (750 degrees Fahr.) except a change which can be attributed to crystal growth. The suggestion which has been made that substantially all of the solid phase transitions may be attributed to the sluggish nature of reactions in manganese alloys may be definitely rejected because in many of the alloys, several definite microstructures are revealed in heating from room temperature up to the melting point. In certain instances, the alloy passes from a single phase structure into a definite 2-phase structure and then at higher temperatures back to a single phase structure. This is true for example of the 80.1 per cent alloy. It is impossible to attribute such a series of microstructures to a lag in reaching equilibrium conditions of the alloy which according to all of the current diagrams would be a mixture of solid solution and alpha manganese. A variety of etching agents have been tried for the alloys. Those containing less than 55 per cent manganese could be satisfactorily etched with a solution of potassium dichromate in 8 per cent sulphuric acid. The alloys containing more than 55 per cent manganese were etched with either citric or acetic acid or a mixture of sulphuric acid and glycerin.

Results of Examination of Microstructure

In Table I, we have shown the microstructure of 20 compositions ranging from 12.5 to 97 per cent manganese. These microstructures are illustrated by typical examples shown in Figs. 1 to 17. In Fig. 18 are shown photomicrographs from 91 to 98 per cent manganese of the slowly cooled alloys.

Structure of the Alloys When Quenched from Temperatures Near the Solidus

Early diagrams representing the manganese-copper system indicated that this system was a continuous series of solid solutions with a minimum melting point at approximately 40 per cent manganese. Later investigations, however, indicated that there was little liklihood that the system was of this simple type. The investigations of Persson[2] showed that by the addition of copper to the face-centered tetragonal gamma manganese, the axial ratio was increased to unity at approximately 81 per cent manganese and the crystal structure

[2]Elis. Persson, "X-ray Analysis of the Copper-Manganese Alloys," *Zeit. für physik. Chem.*, Abt. B, Vol. 9, 1930, p. 25.

Table I

Structure of Alloys After Heat Treatment

Composition % Mn	Slowly Cooled	Heated Two Hours and Quenched — Degrees Cent. — 350	400	450	500	600	700	800	900	Quenched
96.2	2-Phase $\alpha + \epsilon$ See Fig. 18	2-Phase $\alpha + \epsilon$ See Fig. 17	2-Phase $\alpha + \epsilon$ Similar to Fig. 17	2-Phase $\alpha + \epsilon$ Similar to Fig. 17	2-Phase $\alpha + \epsilon$ Similar to Fig. 17	2-Phase $\alpha + \epsilon$ Similar to Fig. 17	2-Phase $\gamma + \epsilon$ Similar to Fig. 6	2-Phase $\gamma + \beta$		1100° Single γ Phase Similar to Fig. 3
94.0	2-Phase $\alpha + \epsilon$ See Fig. 18	2-Phase $\alpha + \epsilon$ See Fig. 16	2-Phase $\alpha + \epsilon$ Similar to Fig. 16	2-Phase $\alpha + \epsilon$ Similar to Fig. 16	2-Phase $\alpha + \epsilon$ Similar to Fig. 16	2-Phase $\alpha + \epsilon$ Similar to Fig. 16 except with considerably less α Mn.	2-Phase $\gamma + \epsilon$ See Fig. 6	2-Phase $\gamma + \beta$		1075° Single Phase γ Similar to Fig. 3
91.7	2-Phase $\alpha + \epsilon$ Trace of See Fig. 18	Single Phase ϵ	Single Phase ϵ	2-Phase $\alpha + \epsilon$ $\alpha + \epsilon$ See Fig. 15	2-Phase $\alpha + \epsilon$ Similar to Fig. 15	2-Phase $\alpha + \epsilon$ Similar to Fig. 15 except with smaller amount of α Mn.	2-Phase $\gamma + \epsilon$ Similar to Fig. 6	2-Phase $\gamma + \beta$ See Fig. 20		1050° Phase γ Similar to Fig. 3
90.3	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	2-Phase $\alpha + \epsilon$ Similar to Fig. 15	2-Phase $\alpha + \epsilon$ Similar to Fig. 15	2-Phase $\alpha + \epsilon$ Similar to Fig. 15 except with smaller amount of α Mn.	2-Phase $\gamma + \epsilon$ Similar to Fig. 5	2-Phase $\gamma + \beta$ See Fig. 20		1025° Single Phase γ Similar to Fig. 3
87.2	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	2-Phase $\alpha + \epsilon$ Similar to Fig. 15	2-Phase $\alpha + \epsilon$ See Fig. 14	2-Phase $\alpha + \epsilon$ Similar to Fig. 15 except with smaller amount of α Mn.	2-Phase $\gamma + \epsilon$ Similar to Fig. 5	Single Phase γ See Fig. 20		1000° Single Phase γ Similar to Fig. 3

Table I—Continued
Structure of Alloys After Heat Treatment

Composition % Mn	Slowly Cooled	Heated Two Hours and Quenched — Degrees Cent. 350	400	450	500	600	700	800	900	Quenched
85.2	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	2-Phase $\alpha + \epsilon$ Similar to Fig. 15 very small amount α Mn.	2-Phase $\alpha + \epsilon$ Similar to Fig. 14	Single Phase ϵ Similar to Fig. 9	2-Phase $\gamma + \epsilon$ See Fig. 5	Single Phase γ See Fig. 20		975° Single Phase γ Similar to Fig. 3
82.4	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	2-Phase $\alpha + \epsilon$ Similar to Fig. 13	2-Phase $\alpha + \epsilon$ Similar to Fig. 13	Single Phase ϵ Similar to Fig. 9	2-Phase $\gamma + \epsilon$ Similar to Fig. 5	Single Phase γ Similar to Fig. 3	Single Phase γ See Fig. 3	925° Single Phase γ Similar to Fig. 3
80.1	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	2-Phase $\alpha + \epsilon$ Similar to Fig. 13 small amt. of α Mn.	2-Phase $\alpha + \epsilon$ See Fig. 13	Single Phase ϵ See Fig. 9	2-Phase $\gamma + \epsilon$ Similar to Fig. 5	Single Phase γ Similar to Fig. 3		925° 2-Phase $\delta + \gamma$ Similar to Fig. 2
75.3	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	2-Phase $\alpha + \epsilon$ Similar to Fig. 13 small amt. of α Mn.	2-Phase $\alpha + \epsilon$ See Fig. 12	Single Phase ϵ Similar to Fig. 9	2-Phase $\gamma + \epsilon$ Similar to Fig. 5	Single Phase γ Similar to Fig. 3		850° 2-Phase $\delta + \gamma$ Similar to Fig. 2
70.7	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ Similar to Fig. 8	2-Phase $\gamma + \epsilon$ Similar to Fig. 5	2-Phase $\delta + \gamma$ See Fig. 2		850° 2-Phase $\delta + \gamma$ Similar to Fig. 2
64.9	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	2-Phase $\delta + \gamma$ Similar to Fig. 2	2-Phase $\delta + \gamma$ Similar to Fig. 2		850° 2-Phase $\delta + \gamma$ Similar to Fig. 2
61.3	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ See Fig. 8	2-Phase $\delta + \gamma$ Similar to Fig. 2	2-Phase $\delta + \gamma$ Similar to Fig. 2		850° 2-Phase $\delta + \gamma$ Similar to Fig. 2

Table I—Continued

Structure of Alloys After Heat Treatment

Composition % Mn	Slowly Cooled	Heated Two Hours and Quenched — Degrees Cent. 350	400	450	500	600	700	800	Quenched
55.4	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ Similar to Fig. 11	2-Phase $\delta + \epsilon$ Similar to Fig. 7	2-Phase $\delta + \gamma$ Similar to Fig. 4	2-Phase $\delta + \gamma$ Similar to Fig. 2	850° 2-Phase $\delta + \gamma$ Similar to Fig. 4
49.7	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ	Single Phase ϵ See Fig. 11	2-Phase $\delta + \epsilon$ See Fig. 7	2-Phase $\delta + \gamma$ See Fig. 4	2-Phase $\delta + \gamma$ Similar to Fig. 4	850° 2-Phase $\delta + \gamma$ Similar to Fig. 4
41.9	Single Phase δ Similar to Fig. 10	Single Phase δ Similar to Fig. 10	Single Phase δ Similar to Fig. 10	Single Phase δ Similar to Fig. 10	Single Phase δ Similar to Fig. 10	Single Phase δ Similar to Fig. 10	Single Phase δ Similar to Fig. 1	Single Phase δ Similar to Fig. 1	850° Single Phase δ
35.9	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	850° Single Phase δ
31.1	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	850° Single Phase δ
24.9	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ See Fig. 10	Single Phase δ See Fig. 10	Single Phase δ See Fig. 10	Single Phase δ See Fig. 10	850° Single Phase δ
20.5	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	850° Single Phase δ
12.5	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ	Single Phase δ See Fig. 1	850° Single Phase δ

became face-centered cubic. On the other hand the solid solution of manganese in copper is also face-centered cubic. Some investigators, notably Grube[3] and his co-workers have considered that these two face-centered cubic solid solutions merged indistinguishably into one another so that the system was in fact a continuous series of solid solutions although beyond 81 per cent manganese, there was a gradual change from the cubic lattice of the copper solid solution to the tetragonal lattice of gamma manganese. Most other investigators, however, have indicated a more or less extensive field in which the limiting gamma manganese solid solution coexisted with a saturated solid solution of manganese in copper. Persson[4] drew this field with a very narrow composition range just below 80 per cent but extending in temperatures from approximately 750 to 850 degrees Cent. (1560 degrees Fahr.). Ishiwara[5] on the other hand drew this binary field with a very narrow temperature range, namely from 835 to 850 degrees Cent. (1535 to 1560 degrees Fahr.) extending in composition from approximately 35 to 80 per cent manganese. The X-ray investigations, especially the most recent ones of Grube[6] and his associates indicate that the lattice parameter of the solid solution of manganese in copper increases regularly in approximate conformance with Vegard's law up to about 45 per cent manganese. Beyond this the lattice parameter remains constant up to the region of the gamma solid solution at 80 per cent manganese. The similarity in weight of the copper and manganese atoms prevents an accurate determination of the distribution of these atoms. There would presumably be, however, a difference in the distribution of the copper and manganese atoms in the alloys which follow Vegard's law and those having a nearly constant lattice parameter regardless of composition. In this particular case, it would appear that microscopic examination yielded information which cannot be obtained by the X-ray spectrograph. An examination of the tabulation of our results of micro-examination indicates that the composition range in which the lattice parameter remains constant, namely from approximately 45 to 80 per cent manganese, the alloys possess a dis-

[3]G. Grube, E. Oestreicher and O. Winkler, "The System Copper-Manganese," *Zeit. für Electrochem*, Vol. 45, 1939, p. 776.

[4]Elis. Persson, "X-ray Analysis of Copper-Manganese Alloys," *Zeit. für physik. Chem.*, Abt. B, Vol. 9, 1390, p. 25.

[5]T. Ishiwara, "On Equilibrium Diagrams of the Aluminium-Manganese, Copper-Manganese and Iron-Manganese Systems," Reports of the Tohoku Imperial University, Series 1, Vol. 19, No. 5, 1930, p. 449.

[6]G. Grube, E. Oestreicher and O. Winkler, "The System Copper-Manganese," *Zeit. für Electrochem*, Vol. 45, 1939, p. 776.

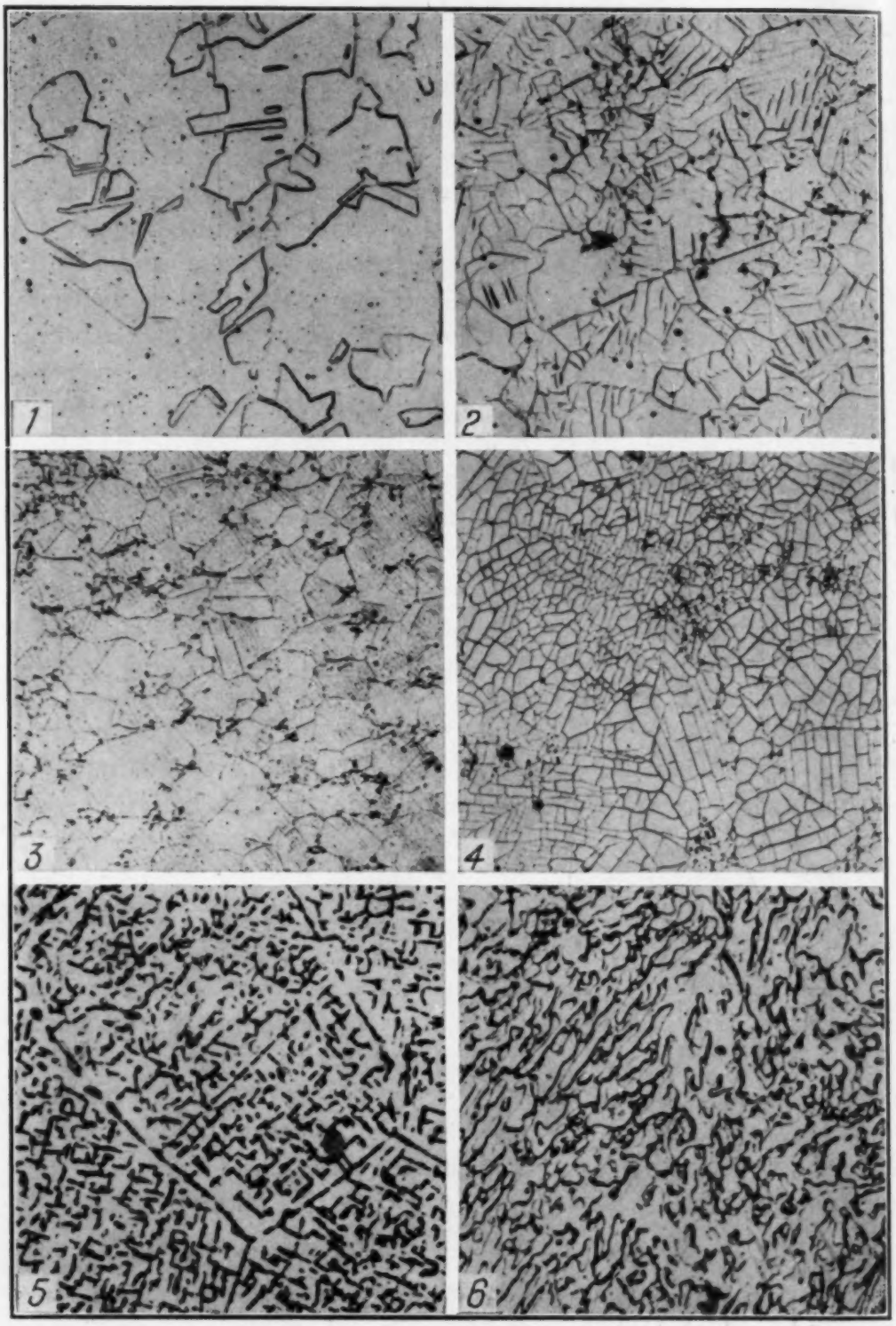

Fig. 1—Manganese 20.5 Per Cent 800 Degrees Cent. × 150.
Fig. 2—Manganese 70.7 Per Cent 800 Degrees Cent. × 125.
Fig. 3—Manganese 82.4 Per Cent 900 Degrees Cent. × 125.
Fig. 4—Manganese 49.7 Per Cent 700 Degrees Cent. × 125.
Fig. 5—Manganese 85.2 Per Cent 700 Degrees Cent. × 750.
Fig. 6—Manganese 94.0 Per Cent 700 Degrees Cent. × 750.

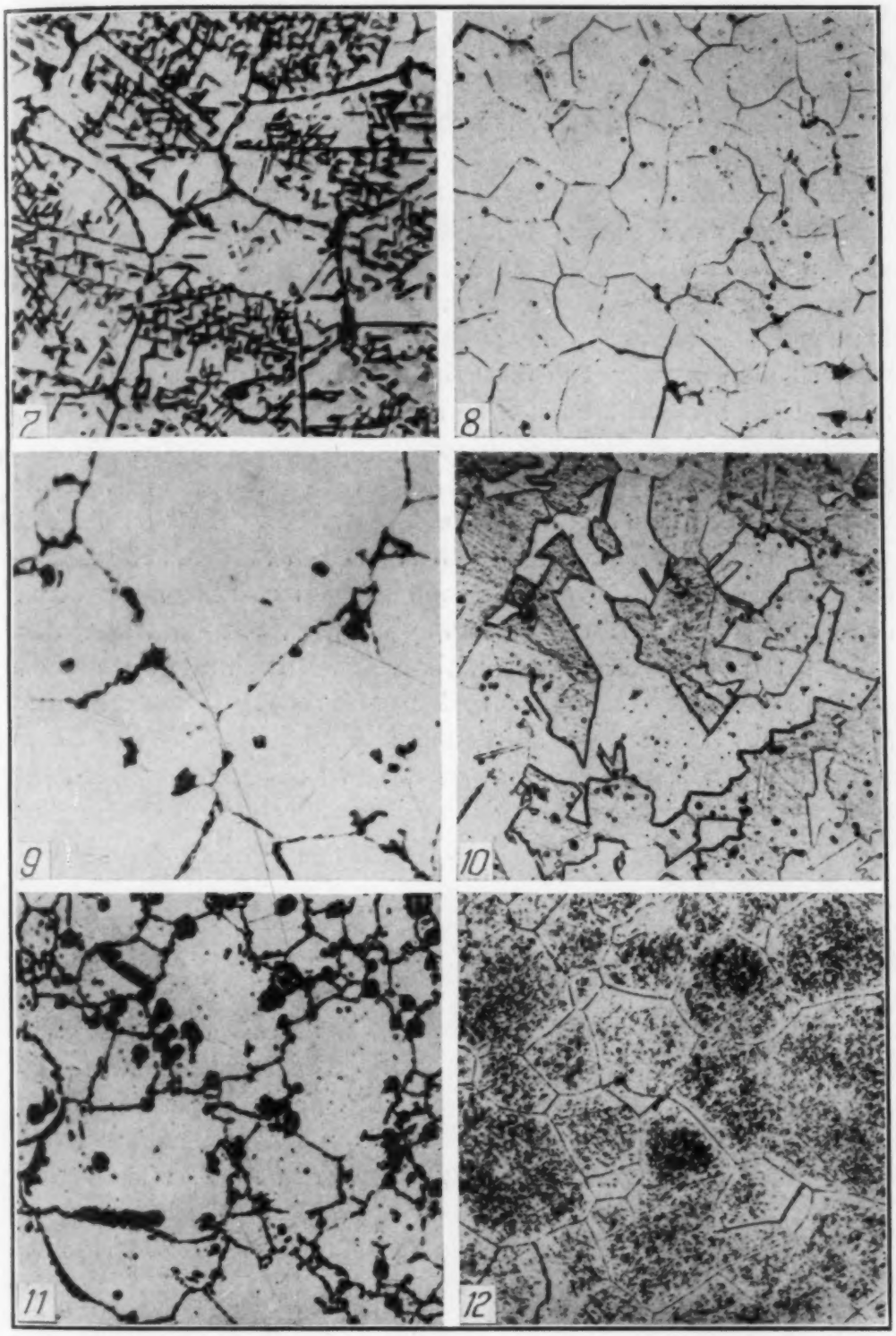

Fig. 7—Manganese 49.7 Per Cent 600 Degrees Cent. × 750.
Fig. 8—Manganese 61.3 Per Cent 600 Degrees Cent. × 150.
Fig. 9—Manganese 80.1 Per Cent 600 Degrees Cent. × 750.
Fig. 10—Manganese 24.9 Per Cent 500 Degrees Cent. × 150.
Fig. 11—Manganese 49.7 Per Cent 500 Degrees Cent. × 250.
Fig. 12—Manganese 75.3 Per Cent 500 Degrees Cent. × 250.

tinctive microstructure. This structure is clearly illustrated in Figs. 2 and 4. The structure shown in Fig. 4 may be considered as a development of that shown in Fig. 2. This structure is an unusual one in alloy systems. We have been unable to find any published photomicrographs showing exactly this kind of block structure and are unable to offer an entirely satisfactory explanation of this structure, but it would appear to have its counterpart in certain intergrowths common in salt crystals and minerals. These intergrowths result from preferential development of a crystal face common to both lattices. We are inclined to the view that the saturated gamma solid solution of copper in manganese and the saturated solution of manganese in copper are not truly isomorphous, and that the peculiar structure shown in Fig. 4 is in reality a type of eutectic. Further studies are now in progress to determine the relationship between the veining as shown in Fig. 2 and the block structure in Fig. 4. This will appear in a later paper. We therefore conclude that the 2-phase field in which the two types of solid solution co-exist has approximately the composition range given by Ishiwara[7] and the temperature range given by Persson.[8] If this is the case, the manganese-copper system becomes an example of Roozeboom's[9] Type IV commonly illustrated by the system cadmium-mercury. The shape of the solidus as determined by various investigators and summarized by Hansen[10] lends considerable support to this interpretation of the diagram. Our studies of electrical resistance[11] previously reported are also in conformity with a diagram of this type. The change of electrical resistance with composition in both the gamma solid solution range and the solid solution of manganese in copper up to 45 per cent manganese is linear. These two linear portions of the composition resistance curve are connected by a curve passing through a maximum between 60 and 65 per cent manganese which is approximately the center of the composition range where the two types of solid solution are postulated to co-exist. The reason for this maximum rather than a constant resistance throughout this 2-phase region must be related in some way to the peculiar type of intergrowth which is present.

[7]T. Ishiwara, "On Equilibrium of Aluminium-Manganese, Copper-Manganese and Iron-Manganese Systems," Reports of the Tohoku Imperial University, Series I, Vol. 19, No. 5, 1930, p. 449.

[8]Elis. Persson, "X-ray Analysis of Copper-Manganese Alloys," *Zeit. für physik. Chem.*, Abt. B, Vol. 9, 1930, p. 25.

[9]H. W. B. Roozeboom, *Zeit. für physik. Chem.*, Vol. 30, 1899, p. 385.

[10]M. Hansen, "Der Aufbau der Zweistofflegierungen," Julius Springer, Berlin, 1936.

[11]R. S. Dean and C. Travis Anderson, "The Alloys of Manganese and Copper: Electrical Resistance," TRANSACTIONS, American Society for Metals, Vol. 29, 1941, p. 788.

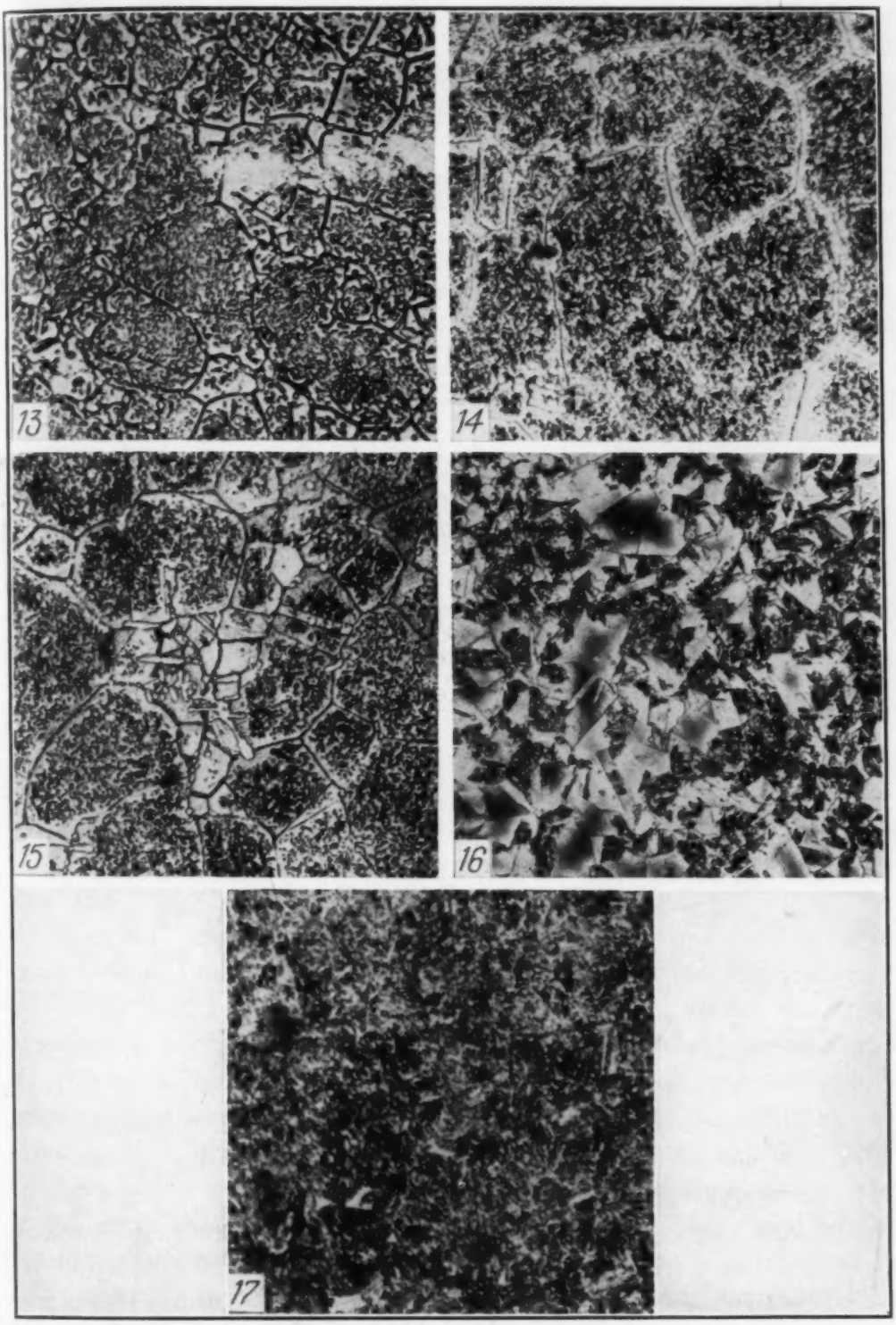

Fig. 13—Manganese 80.1 Per Cent 500 Degrees Cent. × 250.
Fig. 14—Manganese 87.2 Per Cent 500 Degrees Cent. × 250.
Fig. 15—Manganese 91.7 Per Cent 450 Degrees Cent. × 325.
Fig. 16—Manganese 94.0 Per Cent 350 Degrees Cent. × 125.
Fig. 17—Manganese 96.2 Per Cent 350 Degrees Cent. × 200.

Microstructure of the Slowly Cooled Alloys

All of the currently proposed diagrams of manganese-copper alloys indicate that the slowly cooled alloys containing more than 30 per cent manganese would be a mixture of the solid solution of manganese in copper and alpha manganese. The evidence on which this conclusion rests is, however, substantially negligible. The assumption seems to be that any failure of the experimental results to coincide with this conclusion is due to insufficiently slow cooling and consequent failure to attain equilibrium. We have not conducted experiments with extremely slow cooling or long time heating at low temperatures. There is nothing, however, in any of our experiments to indicate that alpha manganese ever separates from an alloy containing less than 70 per cent manganese. The slowly cooled alloys containing up to and including 42 per cent manganese show the typical twinned structure of copper solid solutions. This area we have designated as delta. This structure is the same whether the alloys are quenched, slowly cooled or heated to intermediate temperatures. The solid solution of manganese in copper, therefore, appears to be stable at ordinary temperatures up to approximately 42 per cent manganese. Between this point and 92 per cent manganese the slowly cooled alloys appear to be a single phase. We have termed this phase epsilon. These slowly cooled alloys show no twinning or evidence of the type of intergrowth found in these alloys when quenched. At about 92 per cent manganese the slowly cooled alloys become definitely 2-phase. The second phase has been identified by X-ray spectrometry as alpha manganese. These alloys therefore consist of the alpha and epsilon phases. These transitions are clearly shown in Fig. 18. It can be seen that in the 92 per cent manganese alloy there is a trace of a second constituent which increases as the percentage of manganese increases up to 98 per cent manganese, at which point the alloy becomes single phase. This indicates that there is solid solution of copper in alpha manganese up to 2 per cent copper. This is contrary to the observations of the other investigators but is borne out by our own unpublished X-ray studies which show a definite change of the lattice parameter of alpha manganese up to approximately 2 per cent copper. The boundary between the solid solution of manganese in copper and the epsilon phase as well as the boundary between the epsilon phase and the 2-phase region containing alpha manganese are placed by

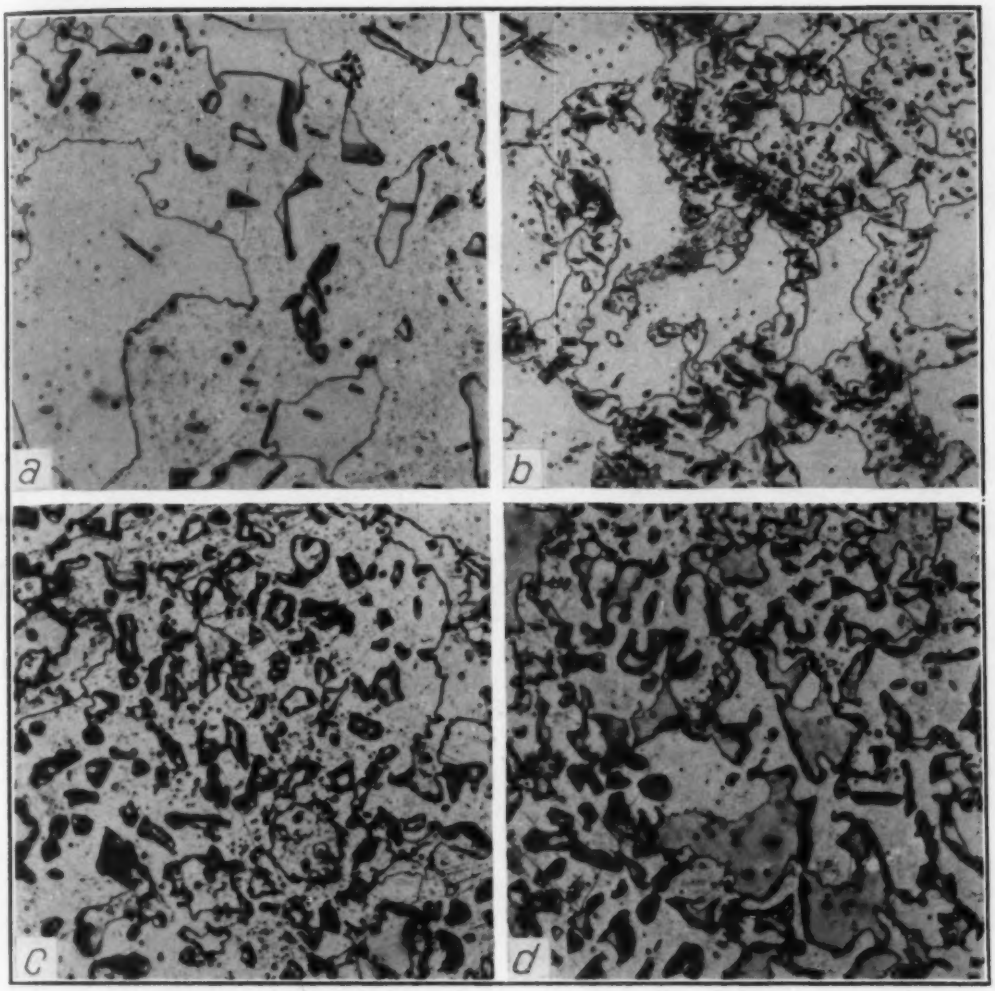

Fig. 18—Manganese-Copper Alloys Heated in Helium for 2 Hours at Indicated Temperatures. Slowly Cooled in Helium for 18 Hours. × 150.

Fig. 18a—Mn 98, Cu 2, 1175 Degrees Cent. Fig. 18b—Mn 97, Cu 3, 1142 Degrees Cent. Fig. 18c—Mn 96, Cu 4, 1100 Degrees Cent. Fig. 18d—Mn 95, Cu 5, 1090 Degrees Cent.

electrical resistance measurements at precisely the same compositions as by a study of microstructure. In our previously published paper on electrical resistance it is shown that the slowly cooled alloys increase smoothly on the addition of manganese to copper up to approximately 40 per cent and that resistance then falls irregularly with increased manganese content until a content of 92 per cent is reached. At this point, the electrical resistance of the quenched and slowly cooled alloys are the same. Beyond this point the slowly cooled alloys show a sharp increase in resistance, a definite indication that alpha manganese has appeared as a constituent. Microstructure alone naturally gives no information concerning the nature

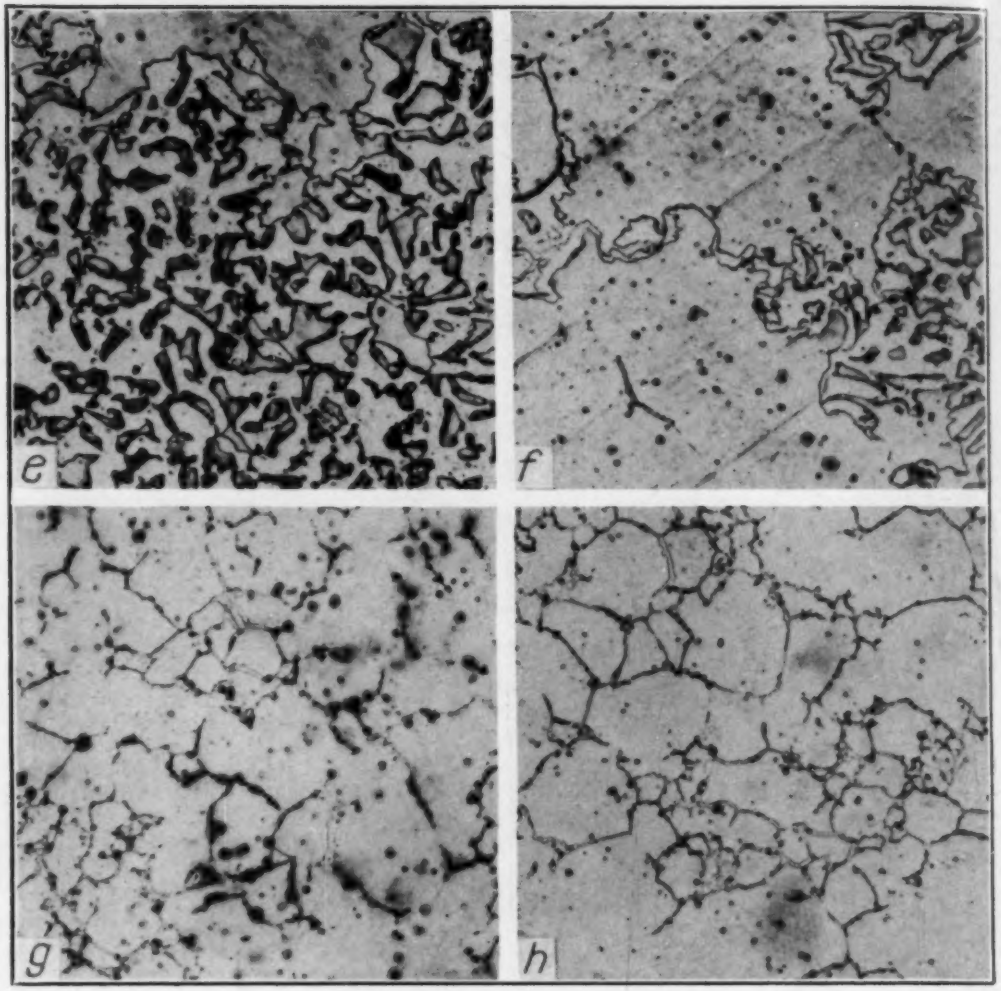

Fig. 18—Manganese-Copper Alloys Heated in Helium for 2 Hours at Indicated Temperatures. Slowly Cooled in Helium for 18 Hours. × 150.

Fig. 18e—Mn 94, Cu 6, 1075 Degrees Cent. Fig. 18f—Mn 93, Cu 7, 1060 Degrees Cent. Fig. 18g—Mn 92, Cu 8, 1050 Degrees Cent. Fig. 18h—Mn 91, Cu 9, 1040 Degrees Cent.

of the epsilon phase. In our paper on electrical resistance, as well as our paper on vibration damping capacity of these alloys, we have suggested that the epsilon phase is a series of ordered lattices having the structure of the solid manganese in copper. The lattice parameter studies of Grube and his co-workers on alloys heated to 400 degrees Cent. (750 degrees Fahr.) indicated that throughout the epsilon range the lattice parameter is constant but is definitely less than that of the quenched alloys in the same composition range. From this we may suggest that the mixture of delta and gamma solid solutions which exists at high temperatures passes on cooling into a single ordered phase. Transitions of this kind are not un-

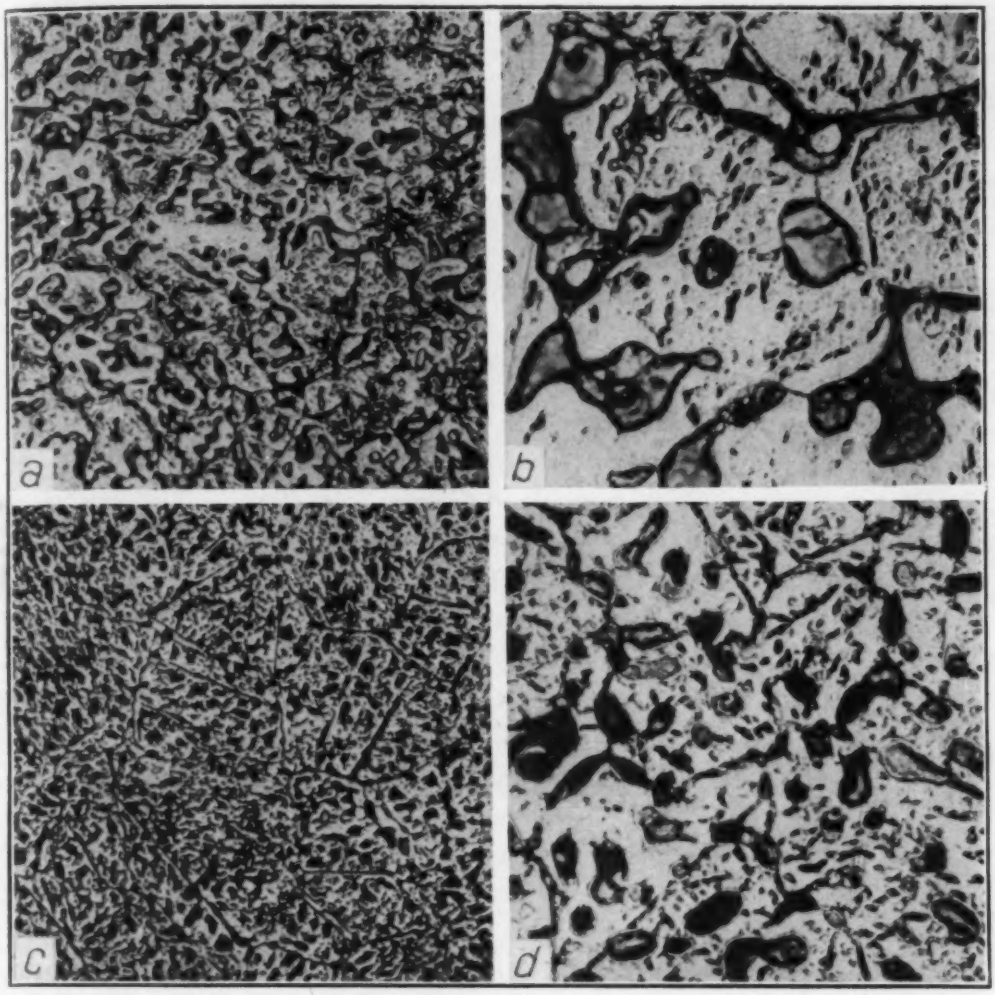

Fig. 19—Manganese-Copper Alloys Heated for 2 Hours at 800 Degrees Cent. Quenched. Fig. 19a—Mn 91.7. × 150; Fig. 19b—Mn 91.7. × 500; Fig. 19c—Mn 90.3. × 150; Fig. 19d—Mn 90.3. × 500.

common in metallurgical systems. Alloys of iron and nickel in the permalloy range, that is around 78 per cent nickel are unstable mixtures of the iron and nickel lattices but with suitable heat treatment are transformed into the ordered lattice of the highly magnetic permalloy. Due to the similarity in atomic weight of copper and manganese, it is not easy to show by X-ray spectrometry whether or not the epsilon phase is actually an ordered lattice. Work on this is underway, however.

Microstructure of Alloys Reheated After Quenching

As previously pointed out alloys containing less than approximately 42 per cent manganese show no structural change on reheat-

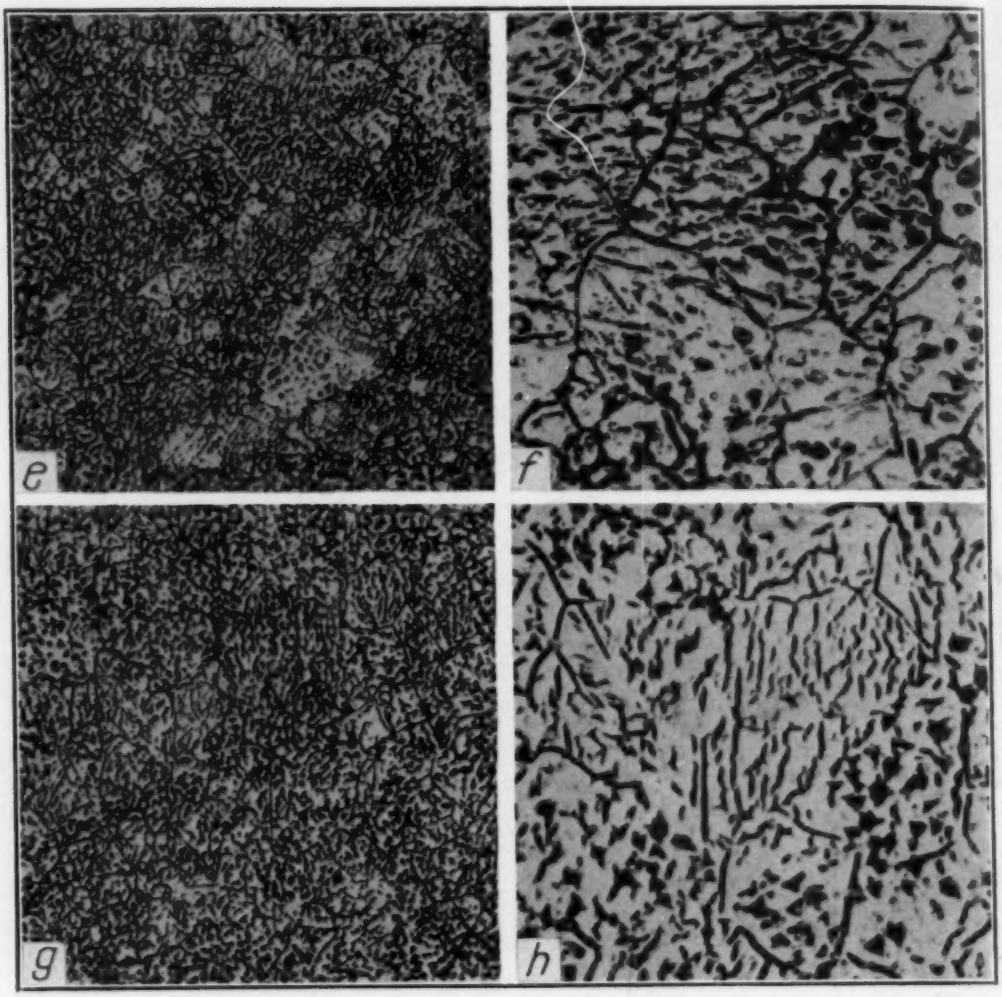

Fig. 19—Manganese-Copper Alloys Heated for 2 Hours at 800 Degrees Cent. Quenched. Fig. 19e—Mn 87.2. × 150; Fig. 19f—Mn 87.2. × 500; Fig. 19g—Mn 85.2. × 150; Fig. 19h—Mn 85.2. × 500.

ing. With alloys containing more than 42 per cent manganese but less than 68 per cent, the epsilon phase when heated to temperatures between 500 and 700 degrees Cent. (930 and 1290 degrees Fahr.) breaks down with the formation of a sort of Widmanstätten structure shown clearly in Fig. 7. On further heating, this structure passes into that of the quenched alloys as shown in Fig. 4. At higher manganese contents the duplex field represented in Fig. 7 becomes very narrow and may disappear entirely between 60 and 70 per cent manganese. In any case the single phase structure of the epsilon phase persists up to 600 and at 700 degrees Cent. (1110 and 1290 degrees Fahr.) the structure of the quenched alloys has again reap-

peared. With alloys containing more than 70 per cent manganese the epsilon phase decomposes at increasingly lower temperatures as can be seen in Table I and until at 92 per cent it is no longer stable in the slowly cooled alloys. This decomposition of the epsilon phase into a mixture of alpha manganese with the epsilon phase is illustrated in Figs. 12, 13, 14, 15, 16 and 17. One of the peculiar features of the diagram, but one which has been checked carefully, is the re-solution of the separated alpha manganese on heating the alloys containing from 70 to 98 per cent manganese to a temperature of 600 degrees Cent. (1110 degrees Fahr.). This re-solution is clearly shown by comparison of Figs. 13 and 9. Conclusive evidence is lacking that the substantially single phase structure of Fig. 9 is identical with that of the epsilon phase shown in Fig. 11. There appears to be no reason, however, for adding an additional phase differing in microstructure from epsilon. On heating any of the alloys above 68 per cent manganese to a temperature of 700 degrees Cent. (1290 degrees Fahr.), a typical two-phase structure is formed, illustrated in Figs. 5 and 6. This we consider to be a decomposition of the epsilon phase into epsilon and the saturated gamma solid solution. This interpretation of the microstructure of these alloys is subject to revision with careful X-ray studies now underway. On heating above 750 degrees Cent. (1380 degree Fahr.), the alloys containing more than 68 per cent manganese pass either into gamma solid solution or into the gamma plus beta field. This transition is clearly shown in Fig. 19 as taking place between 87.2 and 90.3 per cent manganese in the alloys quenched from 800 degrees Cent. (1470 degrees Fahr.). These particular alloys have been etched with a hydrochloric acid solution of ferric chloride. The gamma plus beta phase are shown up to and including 90.3 per cent manganese. The microstructure of the alloys in the gamma plus beta range is very characteristic. At 87.2 per cent manganese the beta phase disappears. This change is also illustrated in the higher magnifications of these alloys. With the ferric chloride etch, veining makes its first appearance in the gamma solid solution field. This part of the diagram is closely in agreement with Persson.

Conclusion

The microstructure of the manganese-copper alloys has been studied after heating for several hours just below the solidus and

quenching and after furnace cooling. The alloys have been studied after heating for several hours just below the solidus and quenching and after furnace cooling. They have also been studied after reheating the quenched alloys to various temperatures. While no claim is made that complete equilibrium was reached in every case, it is felt that the results represent fairly accurately the change which takes place in the heat treatment of the alloys under practical conditions. Further work is now being conducted on the manganese-copper system and will be the subject of later papers.

ACKNOWLEDGMENT

The authors wish to thank R. T. C. Rasmussen for preparing the photomicrographs shown in Figs. 18 and 19.

THE ALLOYS OF MANGANESE-NICKEL AND COPPER

The Electrical Resistance and Temperature Coefficient of Electrical Resistance

By R. S. Dean and C. Travis Anderson

Abstract

The electrical resistance of Mn-Ni-Cu alloys was determined at room temperature and at 100 degrees Cent. From these two resistance values and the temperature interval the temperature coefficient of electrical resistance was calculated and the results tabulated. The resistance of these alloys follows the resistance of the Mn-Cu alloys, the peak occurring between 60-65 per cent manganese. The resistance was measured again after heating to 450 degrees Cent. for 12 hours. The diagram of results shows three different lines where no permanent change in resistance takes place on heating. The largest decrease took place along the pseudo-binary line Cu-MnNi. Other decreases were noted near $MnNi_3$ and the binary alloy Mn-Cu containing 60-65 per cent manganese. An increase, however, was found along the binary Mn-Ni line starting at 67 per cent manganese. Alloys containing as high as 98 per cent manganese can be worked without difficulty when sufficiently pure.

Introduction

IN a previous paper[1] we have discussed the hardening of the alloys having compositions near the pseudo-binary line Cu-MnNi. In the present paper we present the data on the electrical resistance and temperature coefficient of electrical resistance, both before and after heat treating the alloys at 450 degrees Cent. (840 degrees Fahr.) for 12 hours.

Very little previous work has been done on the manganese-nickel-

[1]R. S. Dean, C. Travis Anderson, "The Alloys of Manganese-Nickel and Copper: Hardening in the Pseudo-binary System Cu-MnNi," Transactions, American Society for Metals, Vol. 29, 1941, p. 808.

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Of the authors, R. S. Dean is chief engineer, and C. Travis Anderson is metallurgist, Metallurgical Division, Bureau of Mines, United States Department of the Interior. Manuscript received January 4, 1941.

copper system. Parravano[2] determined the solidus-liquidus points for 36 alloys of manganese-nickel-copper. He worked with Goldschmidt manganese, which contained as impurities 0.99 per cent iron, 0.57 per cent silicon, and 0.53 per cent aluminum. His nickel contained 99 per cent nickel, and the copper used analyzed 99.92 per cent copper. Except for taking a few photomicrographs he made no other measurements on the alloys. Hunter and Sebast[3] in studying the electrical properties of high resistance alloys prepared about 20 manganese-nickel-copper alloys. The highest manganese content of their alloys however was only 13 per cent manganese. Although very few of the alloys we have prepared contain such a low percentage of manganese, the specific resistance given by them in general agrees with the values we have obtained. Shemtchuschny[4] and his co-workers studied a number of alloys in this ternary system. They state, however, that alloys containing more than 30 per cent manganese are somewhat brittle. They found that a ternary alloy consisting of 40 per cent manganese, 20 per cent nickel, and 40 per cent copper reached a resistance of 150 microhms per cubic centimeter. Even with the impure manganese that they used, this value agrees quite closely with the value obtained by us for an alloy of this composition.

The most comprehensive study of the manganese-nickel-copper system which has been made up to the present one is that of Pilling[5] who reported the results he obtained on some 70 alloys. He worked with an extremely impure sample of manganese, analyzing only 94.60 per cent manganese and containing as impurities 1.75 per cent iron, 1.52 per cent silicon, and 1.80 per cent insoluble. He stated that his sample of manganese was an aluminothermic product but apparently no analysis was made for aluminum, although any Al_2O_3 that might be present would be accounted for in the insoluble.

Most of Pilling's alloys were cast in a silica tube, and as a result they probably became contaminated with it, as our previous work has shown that manganese can take up to 10 per cent silica. They probably did not take up anywhere near this amount of silica, as the molten metal was in contact with the silica for such a short time. Carbon was also likely to have been introduced, as the

[2]N. Parravano, "The Ternary Alloys of Iron-Nickel-Manganese, Nickel-Manganese-Copper, Iron-Manganese-Copper," *Internat. Zeit. Metallographie*, Vol. 14, 1913, p. 171.

[3]M. A. Hunter and F. M. Sebast, "The Electrical Properties of Some High Resistance Alloys, *Journal*, American Institute of Metals, Vol. 11, 1917, p. 115.

[4]S. F. Shemtchuschny, S. A. Pogodin and W. A. Finkeisen, "Alloys of High Electrical Resistance," *Ann. Inst. Anal. Phys.-Chim.* (Leningrad), Vol. 2, 1924, p. 405.

[5]N. B. Pilling, "Some Electrical Properties of Copper-Nickel-Manganese Alloys", *Transactions*, American Electrochemical Society, Vol. 48, 1925, p. 171.

alloys were melted in a magnesia crucible in a carbon resistor furnace. As a result of the impurities, all of the alloys above 40 per cent manganese were brittle and those between about 25 and 40 per cent were found to be only deformable. Very recently Kroll,[6] working with double distilled manganese, has prepared a manganese alloy containing 5.1 per cent copper and 8.9 per cent nickel, which he was able to work. We have been able to work without difficulty alloys containing as high as 98 per cent manganese.

Preparation of the Alloys

The alloys were prepared by melting electrolytic manganese which contained not more than 0.02 per cent sulphur and 0.01 per cent iron, with electrolytic nickel and electrolytic copper in a 3 kilovolt-ampere high frequency induction furnace. The melts were made in an alundum crucible, which was backed with granular magnesia, as our earlier work indicated that most other insulating materials were unsatisfactory when melting manganese. No cover or deoxidizer was used, as the alloys were melted quite rapidly. The

Table I

Alloy Number and Composition of Manganese-Copper-Nickel Alloys

Alloy No.	Per Cent Mn	Ni	Cu	Remarks	Alloy No.	Per Cent Mn	Ni	Cu	Remarks
39	65	35	0		66	40	60	0	Brittle
40	65	25	10		67	45	45	10	Brittle
41	65	15	20		68	50	40	10	Brittle
42	65	5	30		69	55	40	5	
43	50	5	45		70	60	40	0	
44	50	15	35		71	45	40	15	
45	50	25	25		74	75	20	5	
46	50	35	15		75	75	15	10	
47	50	45	5	Brittle	76	75	10	15	
48	35	55	10		77	75	5	20	
49	35	45	20		78	65	7½	27½	
50	35	35	30		79	65	2½	32½	
51	35	25	40		80	25	10	65	
52	35	15	50		81	20	20	60	
53	35	10	55		82	20	12½	67½	
54	10	10	80		83	17	17	66	
55	17	17	66		84	15	17½	67½	
56	10	30	60		85	15	15	70	
57	25	25	50		86	12½	25	62½	
58	15	45	40		87	12½	12½	75	
59	19	56	25		88	70	30	0	
60	21	64	15		89	75	25	0	
61	24	71	5		90	80	20	0	
62	25	75	0		91	85	15	0	
63	40	45	15	Brittle	92	80	10	10	
64	40	50	10	Brittle	93	90	5	5	
65	40	55	5	Brittle					

[6] Wilhelm Kroll, "Manganese That Can be Hot Rolled and its Ductile Alloys," *Zeit. für Metallk*, Vol. 31, 1939, p. 20.

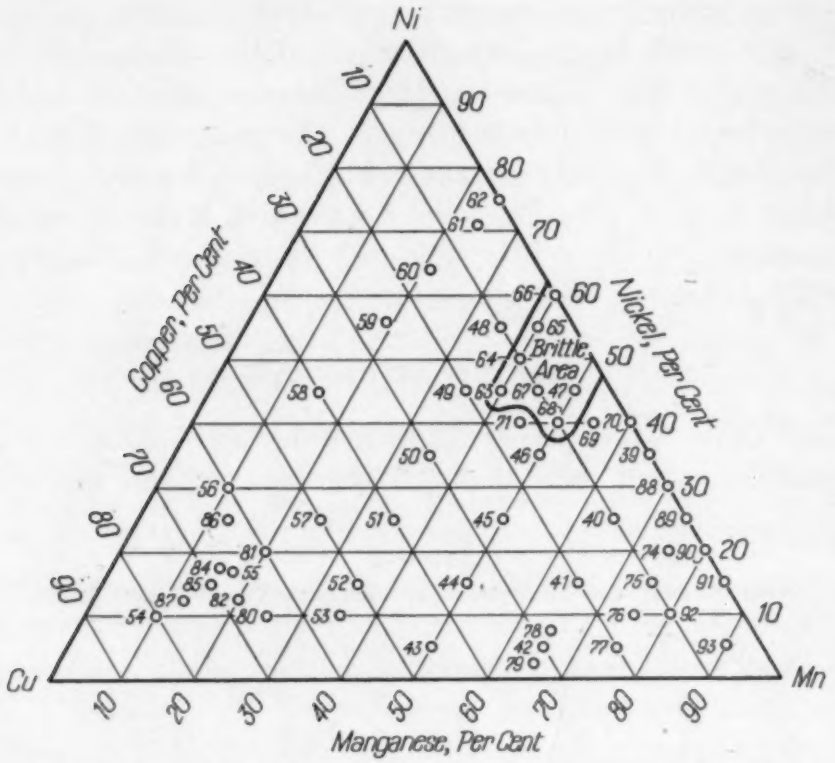

Fig. 1—The Numbers and Composition of the Experimental Alloys.

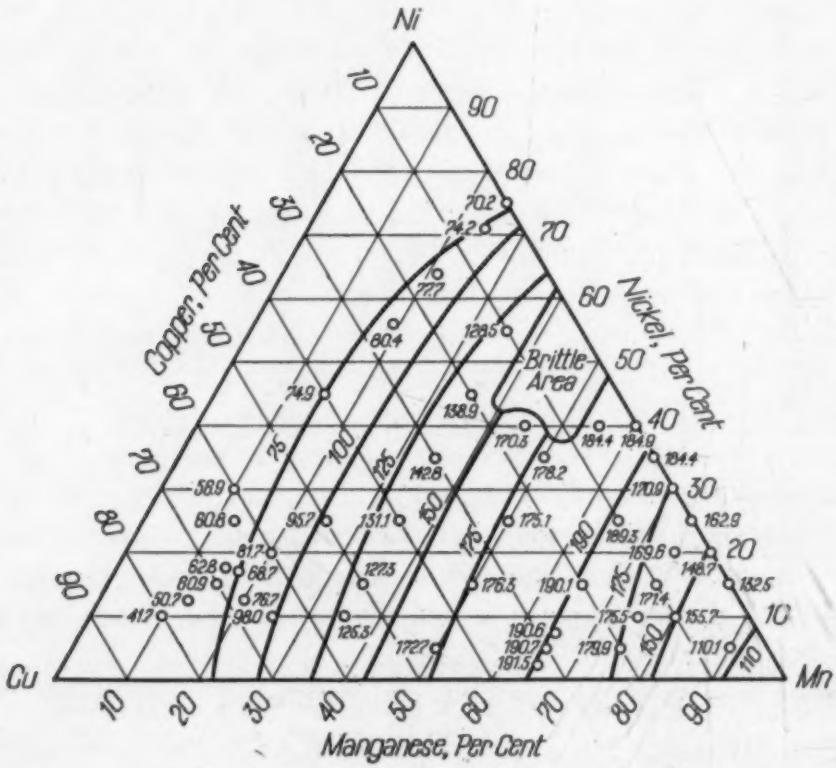

Fig. 2—Specific Resistance of the Manganese-Nickel-Copper Alloys, Ohms $\times$ 10^{-6}/cm^3.

alloys were cast in chill copper molds in ingots 5/8 inch in diameter and 4 inches in length. The alloys were worked down cold by swaging to 0.25 inch in diameter, with intermediate quenches from 900 degrees Cent. (1650 degrees Fahr.).

Table II

Resistance and Temperature Coefficient of Resistance of the Manganese-Nickel-Copper Alloys

Alloy No.	Resistance CW	T°C	Resistance CW	T°C	Temp. Coef. of resistance $\times 10^{-4}$	Resistance after heating to 450°C for 12 hr.	Loss of resistance on heating to 450°C
39	184.4	32.2	184.1	98.4	− 0.2	162.9	11.5
40	189.3	32.2	188.4	98.4	− 0.7	191.5	− 2.3
41	190.1	32.5	190.1	98.4	+ 0	187.8	+ 2.3
42	190.7	32.6	189.4	98.4	− 1.0	149.3	41.4
43	172.7	32.5	171.4	98.4	− 1.1	153.8	18.9
44	176.3	33.0	173.0	98.4	− 2.7	169.3	7.0
45	175.1	32.7	174.2	98.4	− 0.8	171.2	3.9
46	178.2	32.6	175.9	98.4	− 2.0	160.8	17.4
48	128.5	33.0	127.3	98.4	− 1.4	138.2	− 9.7
49	138.9	32.8	137.9	98.4	− 1.1	130.0	+ 8.9
50	142.8	33.0	141.5	98.4	− 1.4	66.3	76.5
51	131.1	32.6	129.7	98.4	− 1.6	94.6	36.5
52	127.3	32.4	126.6	98.4	− 0.8	124.2	3.1
53	125.3	32.6	124.9	98.4	− 0.5	122.7	2.6
54	41.7	32.3	41.4	98.4	− 1.1	40.8	.9
55	68.7	32.2	68.2	98.4	− 1.1	46.5	22.2
56	56.9	26.2	57.4	98.4	+ 1.1	55.9	1.0
57	95.7	27.3	94.8	98.4	− 1.3	60.5	35.2
58	74.9	26.9	75.0	98.4	+ 0.2	74.6	.3
59	80.4	27.4	80.9	98.4	+ 0.9	81.3	− .9
60	77.7	26.5	78.6	98.4	+ 1.6	79.1	− 1.4
61	74.2	26.8	75.7	98.4	+ 2.8	65.4	+ 8.8
62	70.2	27.0	71.9	98.4	+ 3.4	56.2	14.0
69	184.4	26.8	181.7	98.4	− 2.0	158.1	26.3
70	184.9	27.9	184.2	98.4	− 0.5	160.0	24.9
71	170.3	28.0	168.1	98.4	− 1.3	95.6	74.7
74	169.6	25.0	174.0	100.6	+ 3.5	173.6	− 4.0
75	171.4	25.0	175.2	100.6	+ 2.9	172.3	− .9
76	175.5	25.0	178.5	100.6	+ 2.3	171.1	+ 4.4
77	179.9	25.0	181.9	98.7	+ 1.5	157.8	22.1
78	190.6	25.0	189.5	98.7	− 0.8	168.1	22.5
79	191.5	25.0	191.1	98.7	− 0.3	149.7	41.8
80	98.0	25.0	97.8	98.7	− 0.3	94.6	3.4
81	81.7	25.0	81.4	98.7	− 0.5	76.3	5.4
82	76.7	25.0	76.3	98.7	− 0.7	72.7	4.0
83	69.6	25.0	69.1	98.7	− 1.0	64.5	5.1
84	62.8	25.0	62.8	98.7	+ 0.0	57.5	5.3
85	60.9	25.0	60.9	98.7	+ 0.0	55.4	5.5
86	60.8	25.0	60.8	98.7	+ 0.0	56.7	4.1
87	50.7	25.0	50.7	98.7	+ 0.0	46.6	4.1
88	170.9	25.0	173.2	98.7	+ 1.8	178.5	− 7.6
89	162.9	25.0	166.2	98.7	+ 2.7	166.5	− 3.6
90	148.7	25.0	153.3	98.7	+ 4.2	151.1	− 2.4
91	132.5	25.0	140.4	98.7	+ 8.1	135.5	− 3.0
92	155.7	25.0	162.6	98.7	+ 6.0	154.9	+ .8
93	110.1	25.0	122.4	98.7	+15.2	111.4	− 1.3

Table I gives the alloy numbers and compositions of the alloys, as made. The alloys in the brittle area are also given. In the ternary diagram, Fig. 1, the alloy number and composition of the alloys are shown. The actual chemical analysis for the alloys is not given, but

from previous work it has been found that the analysis calculated from the weights of the materials melted usually does not vary more than a few tenths of one per cent from the chemical analysis.

The Electrical Resistance

The electrical resistance of the manganese-nickel-copper alloys was measured by the usual method of substituting the 0.25-inch rod, which had been measured between knife edges a known distance

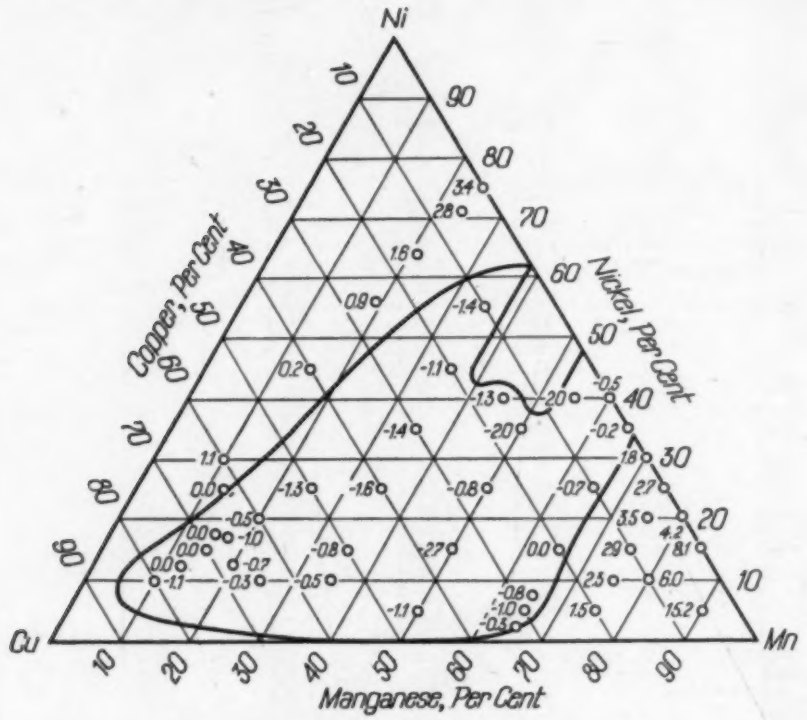

Fig. 3—Temperature Coefficient of Electrical Resistance, Ohms/Ohm × 10^{-4}/°C.

apart, for a standard resistance and measuring the voltage. For this purpose a Type K potentiometer was used. The values of the resistance obtained at room temperature on the cold-worked rods, as well as the results of the measurements on the same rods at approximately 100 degrees Cent., are shown in Table II. The results obtained at room temperature are shown graphically in Fig. 2. From these two resistance values and the temperature interval, the temperature coefficient of electrical resistance was calculated for each of the alloys. We have tabulated these values in the same table and plotted the results on the ternary diagram, Fig. 3. The resistance of

the alloys of this ternary system in general follows the resistance of the manganese-copper alloys. In the binary system manganese-copper the peak of electrical resistance occurs between 60 and 65 per cent manganese, and the same is true of the alloys studied here. After the rods were heated to 450 degrees Cent. (840 degrees Fahr.) for 12 hours the resistance was again measured. The values obtained after this treatment are also shown in Table II. After this heat treat-

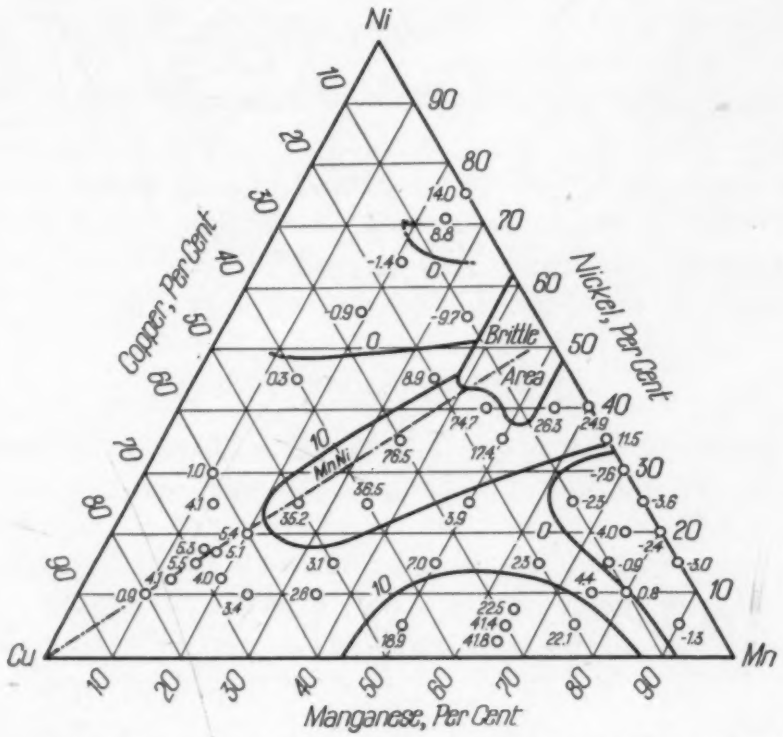

Fig. 4—Decrease in Resistance After Heating the Alloys to 450 Degrees Cent. for 12 Hours. Ohms $\times 10^{-6}/cm^3$.

ment it was noted that a considerable decrease in resistance took place in a large number of the alloys. This decrease is also shown in Table II and has been plotted in Fig. 4. From this figure it may be seen that the largest decrease takes place along the pseudo-binary line Cu-MnNi. A decrease in resistance may also be noted in the neighborhood of the ordered lattice $MnNi_3$ at about 75 per cent nickel. Another area in which a decrease in resistance takes place seems to be influenced by a binary alloy of manganese and copper containing about 60 to 65 per cent manganese, while an area along the binary Mn-Ni line starting from about 67 per cent manganese shows an increase of resistance on heating to 450 degrees Cent. (840 degrees Fahr.) for 12 hours. From this diagram it may be noted

that there are three different lines of thermal stability, i.e., where no permanent change in resistance takes place on heating to 450 degrees Cent.

Exceptionally high resistances similar to those which we have previously reported in the manganese-copper system[7] may be obtained in the manganese-nickel and manganese-nickel-copper systems, with proper heat treatment.

Summary

Ductile alloys have been prepared from electrolytic manganese, nickel and copper containing as high as 98 per cent manganese, and worked down into rods. The electrical resistance and temperature coefficient of electrical resistance have been presented on alloys up to 90 per cent manganese both before and after heating the alloys for 12 hours at 450 degrees Cent. (840 degrees Fahr.).

Acknowledgment

The authors wish to thank V. H. Gottschalk, E. V. Potter and F. M. Bower for assisting in carrying out many of the various measurements.

[7] R. S. Dean and C. Travis Anderson, "The Alloys of Manganese and Copper: Electrical Resistance," Transactions, American Society for Metals, Vol. 29, 1941, p. 788.

THE ALLOYS OF MANGANESE-NICKEL AND COPPER

The Coefficient of Thermal Expansion

By R. S. Dean, C. Travis Anderson and E. V. Potter

Abstract

The coefficient of thermal expansion was measured between 20 and 100 degrees Cent. for Mn-Ni-Cu alloys containing up to 90 per cent manganese in the cold-worked condition, after quenching from 900 degrees Cent. and after heating to 450 degrees Cent. for 12 hours. The latter treatment caused no material change from the cold-worked value. In general, the coefficient of expansion is larger in the quenched than in the cold-worked rods. In both cases the maximum is at approximately 72 per cent manganese where values of above 28 $\times$ 10^{-6} cm/cm/°C were recorded.

IN previous papers of this series we have presented data on the hardening in the pseudo-binary system Cu-MnNi[1] and the electrical resistance and temperature coefficient of electrical resistance[2] of the alloys of manganese, nickel and copper. In this paper we present the results of measurements of the coefficient of thermal expansion of the same alloys. To the best of our knowledge, this property of the manganese-nickel-copper system has not been determined by other investigators.

Preparation of the Alloys

The melting, method of preparing, and heat treating the alloys have been discussed in previous papers[2, 3] and will not be reviewed here. The alloy numbers and their composition are given in Table I.

[1]R. S. Dean and C. Travis Anderson, "The Alloys of Manganese-Nickel and Copper: Hardening in the pseudo-binary system Cu-MnNi," Transactions, American Society for Metals, Vol. 29, 1941, p. 808.

[2]R. S. Dean and C. Travis Anderson, "The Alloys of Manganese-Nickel and Copper: The Electrical Resistance and Temperature Coefficient of Electrical Resistance," Transactions, American Society for Metals, Vol. 29, 1941, p. 899.

[3]R. S. Dean and C. Travis Anderson, "The Alloys of Manganese-Nickel and Copper: Hardening in the pseudo-binary system Cu-MnNi," Transactions, American Society for Metals, Vol. 29, 1941, p. 808.

Of the authors, R. S. Dean is chief engineer, C. Travis Anderson is metallurgist, and E. V. Potter is assistant electrical engineer, Metallurgical Division, Bureau of Mines, United States Department of the Interior, Salt Lake City, Utah. Manuscript received January 4, 1941.

Method of Measurement

The coefficient of thermal expansion was measured by placing the rods, which were approximately 10 inches long and ¼ inch in diameter, in a silica tube sealed at one end. This tube was slightly

Table I

Alloy Number and Analysis of Manganese-Copper-Nickel Alloys

Alloy No.	Per Cent Mn	Per Cent Ni	Per Cent Cu	Remarks	Alloy No.	Per Cent Mn	Per Cent Ni	Per Cent Cu	Remarks
39	65	35	0		66	40	60	0	Brittle
40	65	25	10		67	45	45	10	Brittle
41	65	15	20		68	50	40	10	Brittle
42	65	5	30		69	55	40	5	
43	50	5	45		70	60	40	0	
44	50	15	35		71	45	40	15	
45	50	25	25		74	75	20	5	
46	50	35	15		75	75	15	10	
47	50	45	5	Brittle	76	75	10	15	
48	35	55	10		77	75	5	20	
49	35	45	20		78	65	7½	27½	
50	35	35	30		79	65	2½	32½	
51	35	25	40		80	25	10	65	
52	35	15	50		81	20	20	60	
53	35	10	55		82	20	12½	67½	
54	10	10	80		83	17	17	66	
55	17	17	66		84	15	17½	67½	
56	10	30	60		85	15	15	70	
57	25	25	50		86	12½	25	62½	
58	15	45	40		87	12½	12½	75	
59	19	56	25		88	70	30	0	
60	21	64	15		89	75	25	0	
61	24	71	5		90	80	20	0	
62	25	75	0		91	85	15	0	
63	40	45	15	Brittle	92	80	10	10	
64	40	50	10	Brittle	93	90	5	5	
65	40	55	5	Brittle					

larger in diameter and somewhat longer than the specimen. Another silica tube, approximately the same diameter as the specimen, was fused at one end and ground flat. This second tube was placed in the longer tube to rest on the upper end of the specimen.

A dial gage was clamped to the two tubes in such a manner that any motion of one tube relative to the other could be measured, and the expansion and contraction of the specimen thus determined. The completely assembled apparatus is shown in Fig. 1. By using quartz tubes it was not considered necessary to make any correction for expansion of the tubes, as the correction would be less than the experimental error of the measurements. All the measurements were made from approximately room temperature to about 100 degrees Cent. (210 degrees Fahr.), and the results are expressed as 10^{-6} centimeters per centimeter per degree Cent.

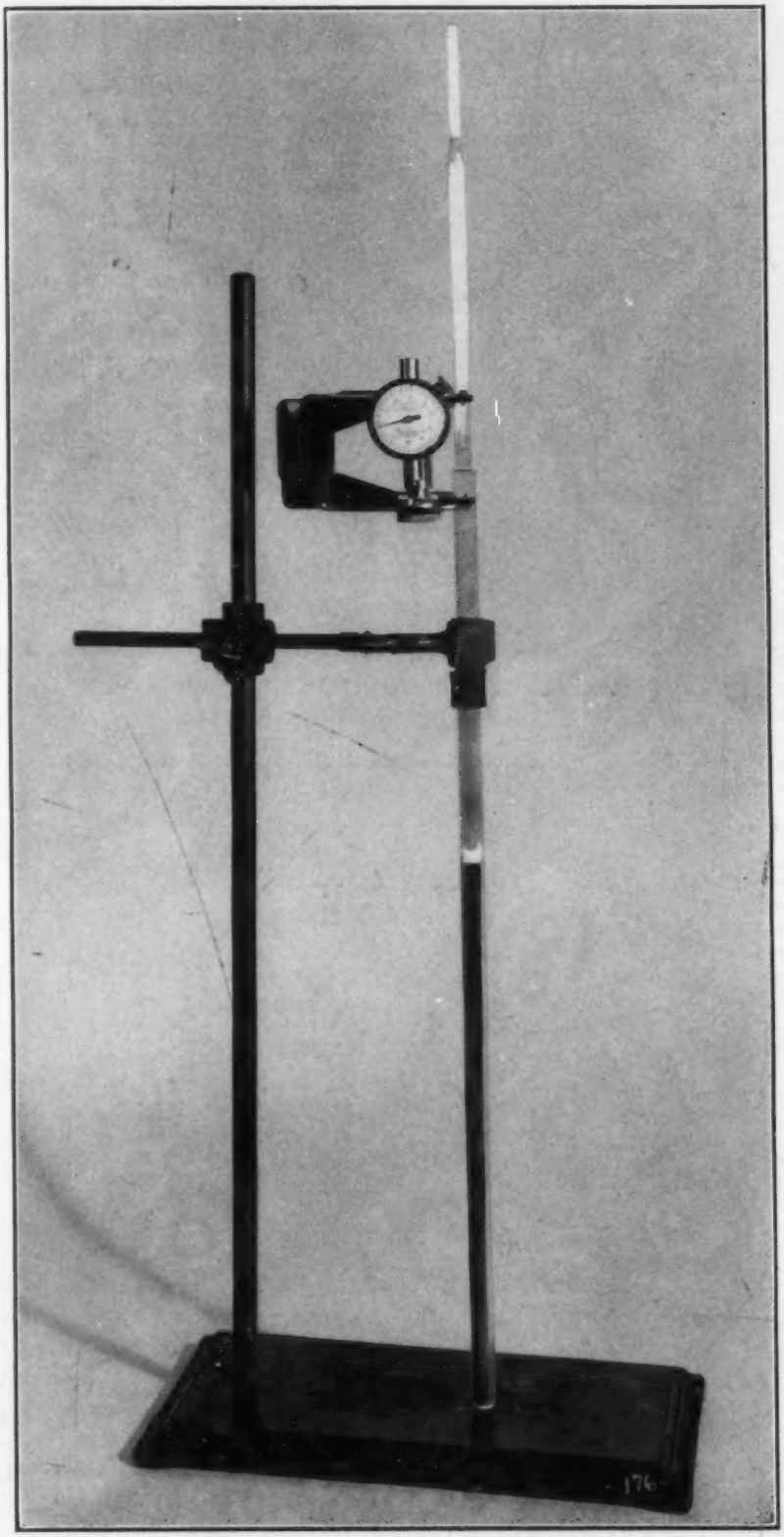

Fig. 1—Apparatus for Determining the Coefficient of Thermal Expansion.

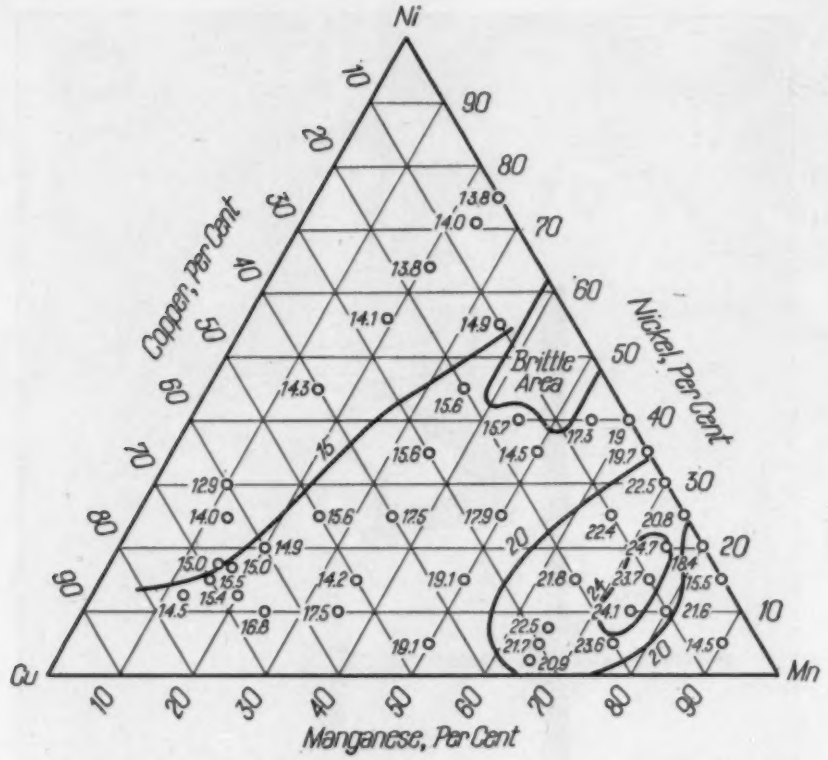

Fig. 2—The Coefficient of Thermal Expansion of the Cold-Worked Manganese-Nickel-Copper Alloys.

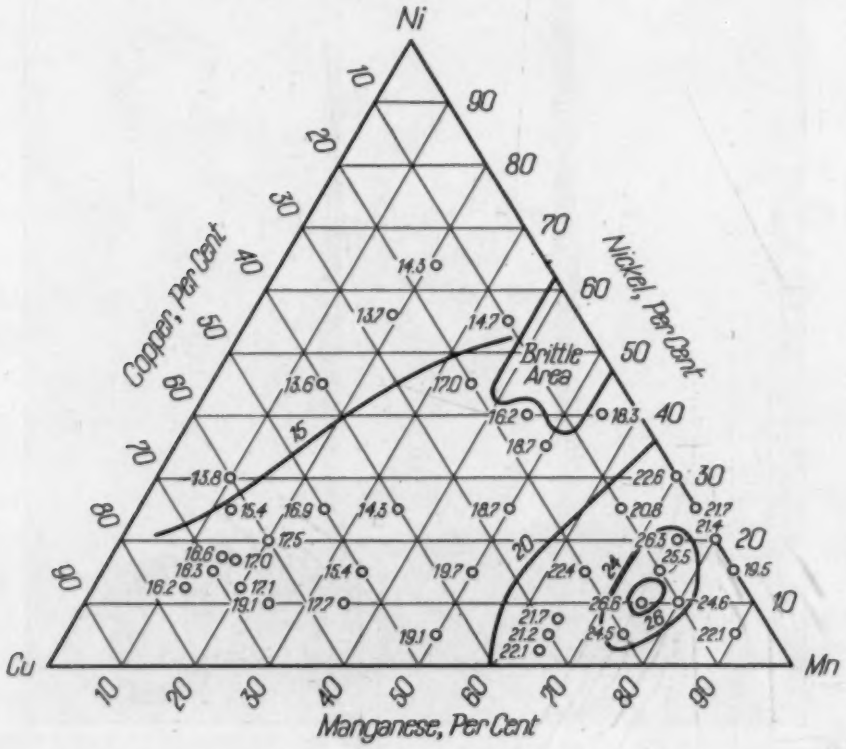

Fig. 3—The Coefficient of Thermal Expansion of the Quenched Manganese-Nickel-Copper Alloys.

The Coefficient of Thermal Expansion

Measurements were made on the specimens in the cold-worked condition, after quenching from 900 degrees Cent. (1650 degrees Fahr.) and on about one-half of the cold-worked rods after being heated to 450 degrees Cent. (840 degrees Fahr.) for 12 hours. From the latter measurements there appeared to be no material change from the cold-worked value. Table II gives the values for mean coefficient of expansion between about 20 and 100 degrees Cent. (75 and 210 degrees Fahr.) for the alloys in both the cold-worked condition and after quenching from 900 degrees Cent. (1650 degrees Fahr.). The values obtained on the cold-worked rods are shown in Fig. 2, while the results obtained on the rods quenched from 900 degrees Cent. (1650 degrees Fahr.) are shown in Fig. 3.

Table II

Coefficient of Thermal Expansion of the Manganese-Nickel-Copper Alloys

Alloy No.	Coefficient of Expansion $\times 10^{-6}$ cm./cm./° C. Cold-worked	After Quenching from 900° C.	Alloy No.	Coefficient of Expansion $\times 10^{-6}$ cm./cm./° C. Cold-worked	After Quenching from 900° C.
39	19.7	....	69	17.3	18.3
40	22.4	20.8	70	19.0	....
41	21.8	22.4	71	15.7	16.2
42	21.7	21.2	74	24.7	26.3
43	19.1	19.1	75	23.7	25.5
44	19.1	19.7	76	24.1	26.6
45	17.9	18.1	77	23.6	24.5
46	14.5	18.7	78	22.5	21.7
48	14.9	14.7	79	20.9	22.1
49	15.6	17.0	80	16.8	19.1
50	15.6	....	81	14.9	17.5
51	17.5	14.3	82	15.4	17.1
52	14.2	15.4	83	15.0	17.0
53	17.5	17.7	84	15.0	16.6
54	15.5	....	85	15.5	16.3
55	14.4	17.4	86	14.0	15.4
56	12.9	13.8	87	14.5	16.2
57	15.6	16.9	88	22.5	22.6
58	14.3	13.6	89	20.8	21.7
59	14.1	13.7	90	18.4	21.4
60	13.8	14.3	91	15.5	19.5
61	14.0	....	92	21.6	24.6
62	13.8	....	93	14.5	22.1

In general, the coefficient of expansion is larger in the quenched than in the cold-worked rods. In both cases the maximum is at approximately 72 per cent manganese. In this region we have recorded values of above 28×10^{-6} centimeters per centimeter per degree Cent.

Summary

The coefficient of thermal expansion between about 20 and 100 degrees Cent. (75 and 210 degrees Fahr.) for manganese-nickel-copper alloys containing up to 90 per cent manganese has been determined on the cold-worked alloys as well as after quenching from 900 degrees Cent. (1650 degrees Fahr.).

Acknowledgment

The authors wish to thank V. H. Gottschalk and F. M. Bower for assisting in carrying out a number of the measurements.

PROPERTIES AND STRUCTURES OF CASE HARDENED STEEL AFFECTED BY COOLING PRACTICE AFTER CARBURIZING

By O. W. McMullan

Abstract

This paper presents the results from tests designed to show the effect of cooling after carburizing on the physical properties of steel subsequently reheated and quenched. From a production viewpoint the purpose was to avoid cooling down to, or near, room temperature in order to save retort space and time in continuous cycles as well as expense in reheating if no loss in physical properties of case hardened parts occurred. Obviously the results are of interest only when direct quenching is not suitable.

S.A.E. 4815 steel was used and specimens were direct quenched, cooled to 1460 degrees Fahr. (795 degrees Cent.) and quenched, and cooled to various temperatures before reheating to single quench from 1460 degrees Fahr. (795 degrees Cent.). Various tests were made on pseudo carburized and hardened specimens and on case hardened specimens. The bend tests described in the paper proved to be the most sensitive to property changes brought about by the cooling cycle. From those tests and subsequent microscopic examination, it was determined that it is unnecessary to cool below the temperature at which the austenitic grain structure is broken up before reheating for hardening. For S.A.E. 4815 this temperature is between 1025 and 900 degrees Fahr. (550 and 480 degrees Cent.). This temperature appears to correspond to the nose of the S-curve and should be similarly located in steels of other compositions.

Introduction

CUSTOMARY procedure has long been to cool carburized work to room temperature or to a relatively low temperature, much below the critical range, before removing the work from the carburizing medium when reheating, rather than direct quenching, is em-

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ployed. Much work is now being put through continuous case hardening cycles where work is quenched direct from the gas carburizing chamber. Some steels, especially those of higher alloy content, do not develop best surface structures and physical properties when direct quenched. Cooling and reheating in such a cycle involves longer retort space and delay and expense in reheating. Desire to lessen these objections led to this investigation to determine the effect of cooling temperature after carburizing on steel to be reheated for quenching. The work was therefore done to aid in a specific production problem rather than from a scientific point of view but it is believed the results justify making a few conclusions even though supported by relatively few results.

The steel used for this investigation was S.A.E. 4815 of the following composition:

	Per Cent
Carbon	0.16
Manganese	0.50
Phosphorus	0.010
Sulphur	0.016
Silicon	0.18
Nickel	3.47
Molybdenum	0.24

The McQuaid-Ehn grain size of the heat was 7 to 8. Core and case properties were determined. Core tests were made on pseudo carburized specimens. Case tests in reality revealed properties of the combined case and core, the case having more or less influence depending on the type of test such as tensile, impact, bend and hardness tests. Solid compound was used for carburizing but it is believed that method of carburizing should have little influence if case depth and carbon concentration are similar.

Core Properties

Billet sections from 3-inch round cornered squares were quartered lengthwise and 1-inch rounds were turned from the quarter sections, thus making them about midway from the corner to the center of the billet. Specimens were long enough for one tensile and one impact test. Test pieces were packed in steel turnings. They were heated to 1700 degrees Fahr. (925 degrees Cent.), held for 9 hours and oil quenched as follows:

1. Direct from 1700 degrees Fahr. (925 degrees Cent.).
2. Cooled slowly to 1460 degrees Fahr. (795 degrees Cent.) and quenched.

3. Cooled to 1250 degrees Fahr. (675 degrees Cent.)—reheated to 1460 degrees Fahr. (795 degrees Cent.) and quenched.
4. Cooled to 1025 degrees Fahr. (550 degrees Cent.)—reheated to 1460 degrees Fahr. (795 degrees Cent.) and quenched.
5. Cooled to 900 degrees Fahr. (480 degrees Cent.)—reheated to 1460 degrees Fahr. (795 degrees Cent.) and quenched.
6. Cooled to 800 degrees Fahr. (425 degrees Cent.)—reheated to 1460 degrees Fahr. (795 degrees Cent.) and quenched.
7. Cooled to 600 degrees Fahr. (315 degrees Cent.)—reheated to 1460 degrees Fahr. (795 degrees Cent.) and quenched.
8. Cooled to Room—reheated to 1460 degrees Fahr. (795 degrees Cent.) and quenched.

After quenching, test bars were drawn at 325 degrees Fahr. (165 degrees Cent.) for 1 hour and machined to standard 0.505-inch tensile test specimens and 10 mm. square Izods. The as-quenched surface hardness of the 1-inch rounds was not changed by the low drawing temperature of 325 degrees Fahr. (165 degrees Cent.).

Table I
Tensile Properties of Pseudo Carburized Bars Heat Treated as 1-Inch Rounds

Treatment Degrees Fahr. Cooled After Carb.	Reheat and Oil Quench	Proportional Limit Lbs. Per Sq. In.	Yield Point Lbs. Per Sq. In.	Maximum Strength Lbs. Per Sq. In.	Per Cent Elong. in 2 Inches	Per Cent Red. Area	Brinell Hardness Center	Brinell Hardness Surface
Quench	*	57500	100000	158250	16	55.7	321	387
1460	*	52500	97000	158000	16	55	321	402–418
1250	1460	50000	91000	149000	17	57.4	302–311	402
1025	1460	50000	88000	144500	18	58.6	302	375
900	1460	52500	91000	147250	18	59.8	302	387-402
800	1460	50000	91000	147500	18.5	61.0	302	375
600	1460	50000	92000	150100	18	61.6	302–311	387–402
Room	1460	52500	92000	151500	18.5	60.7	311	387

*No Reheat.

The center Brinell hardness was taken at the center of the cross section of the large part of the test specimen, the end nearest the fracture being used. This hardness should closely represent that of the metal actually tested.

A strain gage reading to 0.0002 inch was used to obtain readings at every 500-pound load increase. The usual difficulty was encountered in trying to pick a proportional limit, some curves appearing to be more or less continually curved and others having two or more straight sections but at different slopes. No consistency whatever would have been obtained by attempting to draw a straight line through the plotted points. The procedure used was to draw the theoretical line from E = 30,000,000 and calling the

proportional limit as the last point less than 0.0002 inch (one dial division) from the theoretical straight line. Error in reading load and indicator scales was probably somewhat less. Perhaps a figure of about 5000 pounds per square inch less in each case would be more conservative.

Yield point is an arbitrary one obtained by drawing a curve parallel to the theoretical proportional limit to intersect the actual curve at 0.002 inch (0.1 per cent) plastic elongation. No yield point such as shown by dividers or drop of the beam exists in heat treated steel of this type.

Table II
Izod Impact Properties of Pseudo Carburized and Heat Treated Bars

Treatment Degrees Fahr.		Treated as 1-Inch Rounds		Treated as 10 Mm. Square Notched Afterward	
Cooled After Carb.	Reheat and Oil Quench	Foot Pounds	Brinell Hardness	Foot Pounds	Rockwell "C" Hardness
Quench	No reheat	47½, 49½	321–332	47, 46	48–49.5
1460	No reheat	48, 47	321+	.....	.....
1250	1460	56½, 51	302–311	40, 40½	49–50
1025	1460	58½, 61	302	.....	.....
900	1460	60, 59½	302	.....	.....
800	1460	60, 59	302–311	.....	.....
600	1450	64, 64	302–311	46, 48	48.5–50
Room	1460	62, 63	302	.....	.....

Hardness readings were taken on the surface of the test specimens. The hardness of the specimens quenched as 10-mm. squares apparently dropped somewhat below the surface since the corresponding Brinells were a little above 418 or less than conversions from Rockwell readings. The two Izod readings in each case are from single specimens with two notches.

Case Hardened Properties

Izod and bend test specimens were prepared. Two Izod specimens were made fully machined and notched before carburizing in solid compound and heat treating for each of the eight treatments described under core properties. A similar set except without notches was treated for unnotched tests. Bend specimens were first cut to ¾ by 1 inch and 10 inches long, the 1-inch sides being ground. These pieces were then copper plated and two opposite faces machined and ground to leave a ¾-inch square bar 10 inches long copper plated on two opposite sides and, after treatment, case hardened on the other two opposite sides. Three specimens were

made for each of the eight treatments. Bend specimens were cut from a location in the billets similar to that of the tensile tests. Izod specimens also were taken from about the midpoint.

To keep conditions as nearly identical as possible, all the samples, including those pseudo-carburized, were treated at the same time. The two small pots with Izod specimens were put in the carburizing furnace later than the others so that all would come to heat about the same time. This filled the carburizing furnace rather full and it was necessary to remove and shift some of the pots to take out specimens for direct quenching. The pots containing Izod specimens were small and apparently the one with the unnotched specimens cooled below the carburizing temperature more rapidly than the other. That is the only known reason for the case being shallower. After removing the direct quenched samples, all pots were placed back in the furnace which was then allowed to cool. Being heavily loaded, the furnace cooled slowly which accounts for the direct quenched samples having a shallower case than the remainder. The furnace temperature was dropped to and held at 1460 degrees Fahr. (795 degrees Cent.) for some time before the next set of samples was removed and quenched. The furnace was then dropped and held at 1250 degrees Fahr. (675 degrees Cent.). One set of samples was placed in a Hump furnace at 1460 degrees Fahr. (795 degrees Cent.), the remainder were placed in a Homo furnace set at 1025 degrees Fahr. (550 degrees Cent.). By the time the one set was heated, held and quenched from 1460 degrees Fahr. (795 degrees Cent.), the remainder had dropped and were held at 1025 degrees Fahr. (550 degrees Cent.) in the Homo furnace. Another set was taken from the Homo for heating to 1460 degrees Fahr. (795 degrees Cent.), the Homo dropped to 900 degrees Fahr. (480 degrees Cent.), etc., for each successive treatment. Time required for dropping to 1460 degrees Fahr. (795 degrees Cent.) and 1250 degrees Fahr. (675 degrees Cent.) in the larger furnace used for those treatments was 3 to 4 hours each; cycles in the Homo were about one hour each. All test specimens were drawn 1 hour at 325 degrees Fahr. (165 degrees Cent.).

It is quite difficult to measure hardened case depths accurately, especially when the steel is direct quenched or with enough alloy, as in 4815, that the dividing line between case and core is not distinct. The readings given were obtained by polishing and etching all alike in HNO_3 and measuring with a Brinell microscope. Since this

steel hardens completely to a quite low carbon content, case depths are only a little less than total depth of increased carbon content.

Impact Results

Izod specimens were stood vertically in a single row along the sides of small rectangular pots for carburizing, notched specimens in one pot and the unnotched in another. Differences in case depth

Table III

Izod Impact Properties of Case Hardened Specimens. Specimens Completely Machined Before Case Hardening

Treatment Degrees Fahr.		Notched				Unnotched			
Cooled After Carb.	Reheat and Oil Quench	Foot-Pounds	Rockwell "C" Case	Rockwell "C" Core	Case Depth, Inches	Foot-Pounds	Rockwell "C" Case	Rockwell "C" Core	Case Depth, Inches
Quench	No reheat	12	60	38	0.038	51*, 38.5	60-61	40	0.030
Quench	No reheat	14	59.5	39	0.038	43, 40	61	38	0.030
Quench	Avg.	13	59.5	39.5	0.038	40.5	60.5	39	0.030
1460	No reheat	7, 7	59.5	39.5	0.050	35*, 26	60.5-62	38.5	0.045
1460	No reheat	7.5, 8	60	39	0.050	32.5, 34	60.5-62	39.5	0.042
1460	Avg.	7.5	59.5	39.5	0.050	31	61	39	0.043
1250	1460	8, 7.5	59.5	39.5	0.048	36, 36	61.5-63	38.5	0.040
1250	1460	7.5, 8	61-62	39.5	0.050	34, 30	61-62	39	0.040
1250	Avg.	7.5	60.5	39.5	0.049	34	62	39	0.040
1025	1460	8.5, 8	60-61	39.5	0.045	33, 34	62	39	0.040
1025	1460	9, 9	60.5-61	38.5	0.045	34, 29	61-63	39	0.040
1025	Avg.	8.5	60.5	39	0.045	32.5	62	39	0.040
900	1460	8, 8	60-61.5	39	0.050	40.5, 34	61.5-62	38.5	0.035
900	1460	7, 8	60.5	38	0.050	37*, 40	61-62	38.5	0.035
900	Avg.	8	61	38.5	0.050	38	61.5	38.5	0.035
800	1460	9.5, 9	60.5	38.5	0.045	38.5, 30	61-62	39.5	0.035
800	1460	8.5, 8.5	60.5	40	0.045	32, 33	61-63.5	39.5	0.040
800	Avg.	9	60.5	39	0.045	33.5	62	39.5	0.037
600	1460	8.5, 8.5	60.5-61	39.5	0.045	38, 30.5	61.5-62	38.5	0.035
600	1460	8.5, 8	61-61.5	40	0.045	37, 40	61-61.5	39	0.035
600	Avg.	8.5	61	40	0.045	36	61.5	39	0.035
Room	1460	7.5, 7.5	60.5-61	39.5	0.048	39.5*, 36.5*	61.5	39	0.035
Room	1460	8, 8	61-61.5	39	0.050	35.5, 38	61-61.5	39	0.035
Room	Avg.	7.5	61	39.5	0.049	37	61.5	39	0.035

*Broke in grips—readings may be high but only first two are omitted from the average.

apparently were due to the time in cooling between 1700 and 1460 degrees Fahr. (925 and 795 degrees Cent.). Results are given in Table III.

Bend Tests

Bend test specimens were stood vertically all in one large carburizing box. It was necessary to place them in two rows but they were packed so that, in quenching, two specimens were taken from the row next the edge of the box and one from the inner row for

each heat treatment. Because of quicker heating time the outer row might have a slightly deeper case, especially the corner specimen. This box was provided with a thermocouple well in one side and thus readings were taken near the center of the box before removing samples at 1460 and 1250 degrees Fahr. (795 and 675 degrees Cent.).

Tests were made by placing the bars, cased sides on top and bottom, on supports 8 inches apart and loading in the center. Deflection readings were taken at 200-pound load increments and the load at the first crack in the case and maximum load were noted. The direct quenched samples developed two to four cracks in the case; all others broke through the one original crack. Except for the direct quenched specimens and two other cases, the first crack also represented the maximum load carrying capacity. Results are given in Table IV. Stress values are those calculated for outside fibers by the usual bend formula. Stress-strain curves were

Table IV
Results from Case Hardened Bend Test Specimens

Treatment Degrees Fahr. Cooled After Carb.	Reheat and Oil Quench	Deflection at First Crack Lbs. Per Sq. In.	Deflection at 1st Crack, Inches	Max. Load Lbs. Per Sq. In.	Deflection at Max. Load, Inches	Case Depth, Inches	Rock. C of Case	BHN of Core	Remarks
Quench	No reheat	230,450	0.141	258,350	0.197	0.060	54	387	3 cracks in case
Quench	No reheat	230,450	0.139	274,500	0.226	0.055	54–56	387	4 cracks in case
Quench	No reheat	248,900	0.159	258,900	0.182	0.060	54–55	375	2 cracks in case
Quench	Avg.	236,600	0.146	263,900	0.201	0.058	55	383	Coarsest fractures
1460	No reheat	240,400	0.146	244,100	.....	0.070	58–59	387	
1460	No reheat	271,700	0.177	.....	.....	0.060	58–59	375	
1460	No reheat	227,600	0.138	233,300	0.152	0.075	57–58	387	
1460	Avg.	246,600	0.154	238,700	.....	0.068	58	383	Medium fractures
1250	1460	256,600	0.162	.....	.....	0.075	59–60	364	
1250	1460	284,500	0.191	.....	.....	0.065	59	364	
1250	1460	280,200	0.187	.....	.....	0.065	59	364	
1250	Avg.	273,700	0.180	.....	.....	0.068	59	364	Medium fractures
1025	1460	235,400	0.145	.....	.....	0.065	59.5	351	
1025	1460	251,800	0.151	.....	.....	0.065	59–60	351	
1025	1460	251,800	0.153	.....	.....	0.065	59–59.5	351	
1025	Avg.	246,300	0.150	.....	.....	0.065	59.5	351	Medium fractures
900	1460	307,200	0.223	.....	.....	0.060	59	364	
900	1460	318,600	0.245	.....	.....	0.055	60	364	
900	1460	258,900	0.161	.....	.....	0.065	59.5–60	364	
900	Avg.	294,900	0.210	.....	.....	0.060	59.5	364	Fine fractures
800	1460	297,300	0.196	.....	.....	0.060	59	375	
800	1460	328,600	0.249	.....	.....	0.065	59–60	375	
800	1460	326,400	0.235	.....	.....	0.065	59–60	375	
800	Avg.	317,400	0.227	.....	.....	0.063	59.5	375	Fine fractures
600	1460	278,800	0.184	.....	.....	0.065	59–61	364	
600	1460	297,300	0.203	.....	.....	0.065	60–61	364	
600	1460	260,300	0.158	.....	.....	0.070	59.5–61	364	
600	Avg.	278,800	0.182	.....	.....	0.067	60	364	Fine fractures
Room	1460	290,700	0.192	.....	.....	0.065	60–61	364	
Room	1460	315,800	0.230	.....	.....	0.070	61	364	
Room	1460	272,800	0.172	.....	.....	0.065	60	364	
Room	Avg.	293,100	0.198	.....	.....	0.067	60.5	364	Fine fractures

(Note: Where no values are given maximum load occurred at first crack.)

plotted to observe the location of the elastic limit. This appeared to be about 140,000 to 170,000 pounds per square inch, but the total amount of plastic deflection up to the first crack was relatively small. The first four treatments given showed the lowest elastic limits but not as low relatively as the first crack in the case. With the case depths tested, the fiber stress in the core just below the case would be about 5/6 of that of the outside fibers of the case and thus it is quite possible that the plastic deflection occurred largely in the core rather than in the case before it cracked. The copper plate on the sides prevented carbon penetration at the corners more on some samples than others, with the result that some showed a shallower case for a very short distance at the corner. Three samples were purposely used to average such effects, including variations in case depth, surface imperfections, etc. It is believed that the averages given are most representative, but individual results are listed as a matter of interest.

Discussion of Results

Core results on pseudo carburized samples reveal little of significance. Tensile properties run about according to hardness and indicate a slight advantage in reduction of area for cooling to 900 degrees Fahr. (480 degrees Cent.) and below. The same is true for the Izod tests.

Case hardened Izod tests either notched or unnotched also do not reveal any significant differences. It appears that variations observed could readily be accounted for by differences in case depth. Previous tests have shown that case depth is the most important factor in such tests and is much more important than core hardness and small differences in case structure.[1] All cases are so brittle that they crack through very readily under heavy shock loads and thus the test becomes greatly dependent on the area and notch toughness of the core. At similar case depths the properties obtained after all treatments are much alike because the core properties are similar.

The bend tests do show rather decided differences. It is the writer's opinion that except for shallow cases the properties of the case are the determining factors of the overall properties of a case hardened part much more than are those of the core. Since the bend test as conducted was the one best designed to test the properties of

[1] O. W. McMullan, "Physical Properties of Case-Hardened Steels," Transactions, American Society for Metals, Vol. 23, 1935, p. 319.

the case only, it is reasonable to expect that it might be the most sensitive test for determining the effects of the various treatments. It will be observed that the first crack in the case, which might be considered as a measure of useful strength, is decidedly lower for samples not cooled below 1025 degrees Fahr. (550 degrees Cent.) before quenching or reheating for quenching. The direct quenched samples were lowest even though the core was hardest and strongest, which checks with similar tests on the higher alloy steels previously conducted by the writer.[1] The core hardness readings were taken on the fractured ends after grinding and were probably affected by cold work. Checks on several about ½ inch from the fracture gave results about 0.1 mm. or 10 to 12 points lower.

The core fractures of all specimens tested were silky and much alike in appearance. The case fractures of the bend tests showed a difference more difficult to explain. The heat being fine grained, the fracture was not very coarse but the direct quenched cases were crystalline and distinctly coarser than the others. Those quenched direct from 1460 degrees Fahr. (795 degrees Cent.) and those cooled to 1250 and 1025 degrees Fahr. (675 and 550 degrees Cent.) before reheating were finer and nearly alike but distinctly coarser than those first cooled to 900 degrees Fahr. (480 degrees Cent.) or below. The latter were very fine and uniform. Microscopic examinations were made in an attempt to determine the cause of the change in physical properties and case fracture that occurred between the 1025 and 900 degrees Fahr. (550 and 480 degrees Cent.) cooling treatments. Photomicrographs of core and case structures are shown in Figs. 1 to 9. Differences in core structure were not great. The direct quenched samples were a little coarser and more completely martensitic. Others were a little finer grained and showed a less drastic quench with perhaps a trace of ferrite in some boundaries. The acicular pattern in the reheated samples (some also as direct quenched) gives the appearance of coarse pearlite and free ferrite. It is believed that this is actually a Widmanstätten structure with constituents of varying carbon content and different etching rates and not actually free ferrite in the lighter portions. The change that took place in the core structure occurred between the delayed quench from 1460 degrees Fahr. (795 degrees Cent.) and the 900 degrees Fahr. (480 degrees Cent.) reheat, Fig. 4, but mostly between the 1250 and 1025 degrees Fahr. (675 and 550 degrees Cent.) reheats, Figs. 2 and 3.

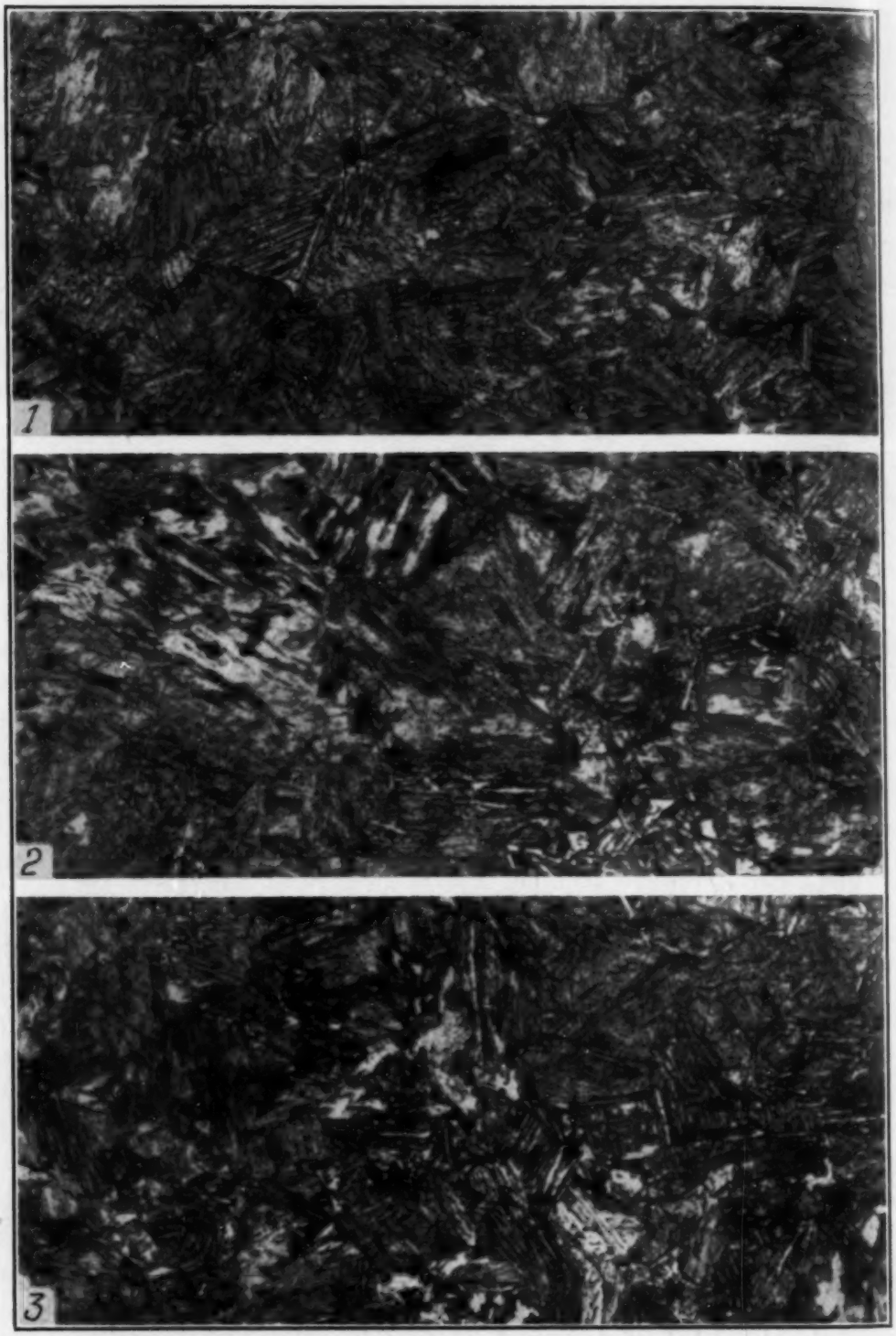

Fig. 1—Core Structure When Direct Quenched from 1700 Degrees Fahr. × 500.

Fig. 2—Core Structure When Cooled to 1250 Degrees Fahr., Reheated to 1460 Degrees Fahr., and Quenched. × 500.

Fig. 3—Core Structure When Cooled to 1025 Degrees Fahr., Reheated to 1460 Degrees Fahr. and Quenched. All Nital Etch. × 500.

Case structures are shown in Figs. 5 to 9. Magnification of × 500 was necessary to reveal details of structure but the area is too small to reveal complete differences in case structure. Short etching revealed a bainite type of structure with light areas in most of the cases which are frequently referred to as austenite and amounting to about 50 per cent in the outer layers of the direct quenched sample. Deeper etching developed an acicular pattern in much of this light area, indicating martensite of differing etching rates. Apparently part of the light area is austenite but the direct quenched samples were the only ones having enough to show much effect on the Rockwell hardness. No further attempts were made to definitely identify the nature of these light etching areas. Figs. 5 to 9 were taken the same distance (about 0.010 inch) from the surface and at the location most typical of differences observed. Fig. 5, direct quenched treatment, shows the coarsest acicular structure. Fig. 6, sample cooled to 1460 degrees Fahr. (795 degrees Cent.) and quenched, has a little finer acicular structure and considerably less austenite. There was less austenite at the surface than at some distance below, perhaps indicating that surface carbon content was reduced by gas equilibrium conditions during the slow cool in the compound to 1460 degrees Fahr. (795 degrees Cent.), since such was not true of the direct quench at 1700 degrees Fahr. (925 degrees Cent.). Fig. 7, sample cooled to 1025 degrees Fahr. (550 degrees Cent.) and reheated to 1460 degrees Fahr. (795 degrees Cent.) for quenching, has a noticeably finer acicular structure than Fig. 6 and has less white constituent. Samples cooled to 1250 degrees Fahr. (675 degrees Cent.) and reheated to 1460 degrees Fahr. (795 degrees Cent.) were between Figs. 6 and 7 in structure but closer to Fig. 7. Fig. 8, sample cooled to 900 degrees Fahr. (480 degrees Cent.) before reheating, has some of the acicular structure and light etching areas but in general has more fine-grained uniform martensite such as Fig. 9, cooled to 800 degrees Fahr. (425 degrees Cent.) before reheating. The 600 degrees Fahr. (315 degrees Cent.) and room temperature cool gave results identical to Fig. 9. The variation in Fig. 8 appears to follow a dendritic pattern in the billet, this treatment apparently being sensitive to minor variations in chemistry. The structure is that of the sample showing lowest strength in Table IV. The other 900 degrees Fahr. (480 degrees Cent.) samples giving higher loads were more uniform and closer to Fig.

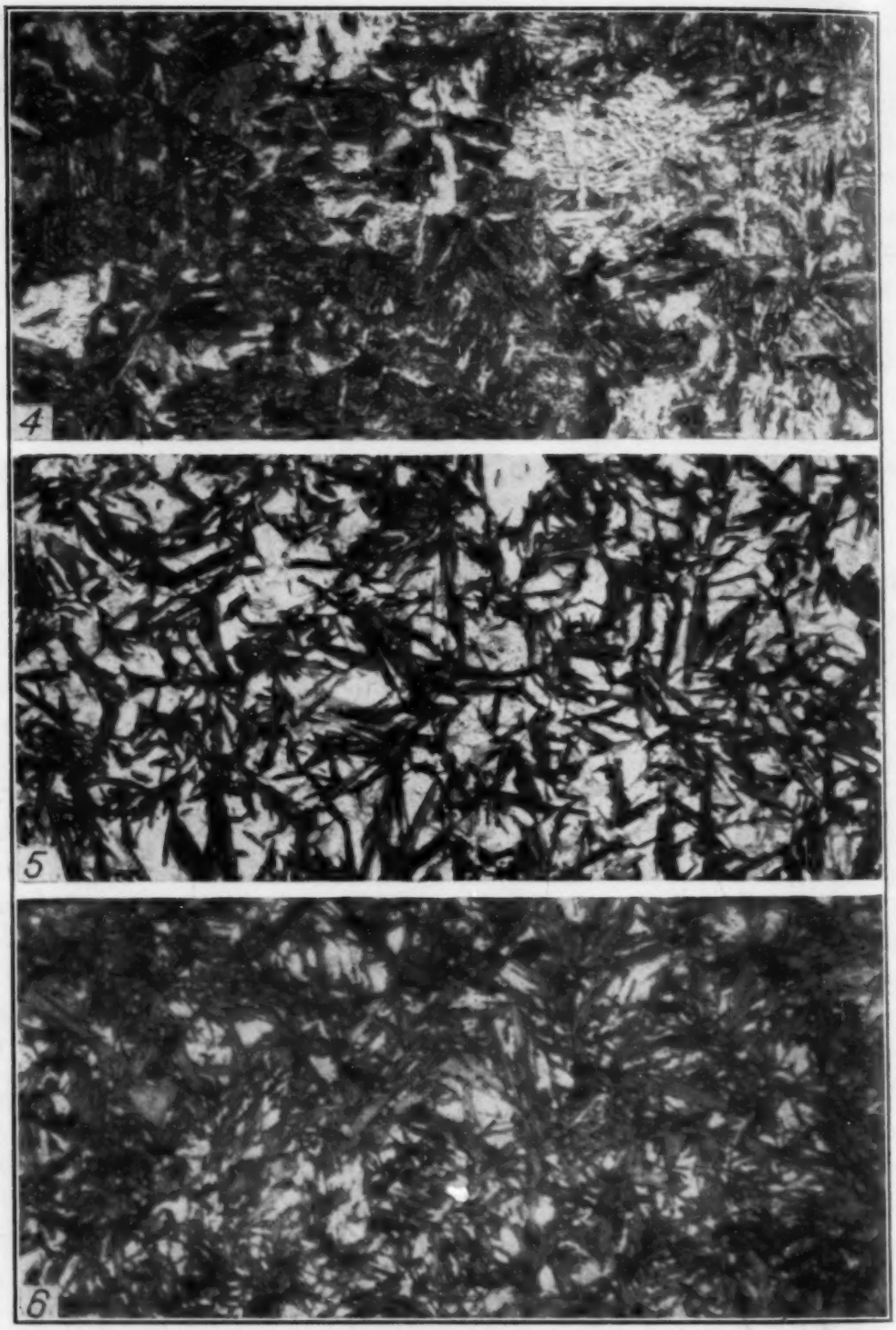

Fig. 4—Core Structure When Cooled to 900 Degrees Fahr., Reheated to 1460 Degrees Fahr., and Quenched. Nital Etch.

Fig. 5—Case Structure When Direct Quenched from 1700 Degrees Fahr. Picral Etch. × 500.

Fig. 6—Case Structure When Cooled to 1460 Degrees Fahr., and Quenched. Picral Etch. × 500.

9 in structure. It was observed that in all samples reheated to 1460 degrees Fahr. (795 degrees Cent.) no light etching constituent was present near the surface. The effect mentioned in connection with Fig. 6 and additional decarburization in reheating to 1460 degrees Fahr. (795 degrees Cent.) are suggested as the reasons. A few small carbides were observed in all treatments except as direct quenched. They are more visible in Fig. 9 because of the dark background. It is believed that their size and distribution are such as to have had no effect on the properties or appearance of fracture.

While the change in case structure is more gradual than the change in physical properties and fracture appearance of the case, the biggest change in structure also occurs between cooling to 1025 degrees Fahr. (550 degrees Cent.) and to 900 degrees Fahr. (480 degrees Cent.). This change is one of a coarser acicular structure to a fine uniform one and to an absence of austenite or light etching martensite. Probably an internal stress change would accompany the changes in structure.

The older conceptions of transformation of steel do not offer a satisfactory explanation for the changes of structure observed. Metals Handbook, page 475, 1939 Edition, lists the Ar_1 point of S.A.E. 4815 and 4820 steel as 800 and 760 degrees Fahr. (425 and 405 degrees Cent.). Since carbon content has little influence on the Ar_1 point, this should represent the point of austenitic decomposition in the case. Changes above this temperature would be only in the amount of excess carbide coming out of solution and in the present case the amount appears to be too small to have much effect. Davenport,[2] shows transformation starting in S.A.E. steels at much higher temperatures. While Davenport does not show decomposition of the 4800 series, other curves indicate that the nose of the S-curve, or high temperature region of most rapid transformation, would probably be a little below 1000 degrees Fahr. (540 degrees Cent.). Transformation according to this pattern conforms to changes shown in Figs. 5 to 9, that is, increasing decomposition of the original coarser-grained acicular pattern, coming from the austenitic structure formed at the carburizing temperature, occurs as the cooling temperature (before reheating) dropped to below 1000 degrees Fahr. (540 degrees Cent.). Rather than being Ae_1 points the temperatures listed as Ar_1 in Metals Handbook appear to be the end of

[2] E. S. Davenport, "Isothermal Transformation in Steels," TRANSACTIONS, American Society for Metals, Vol. 27, 1939, p. 837.

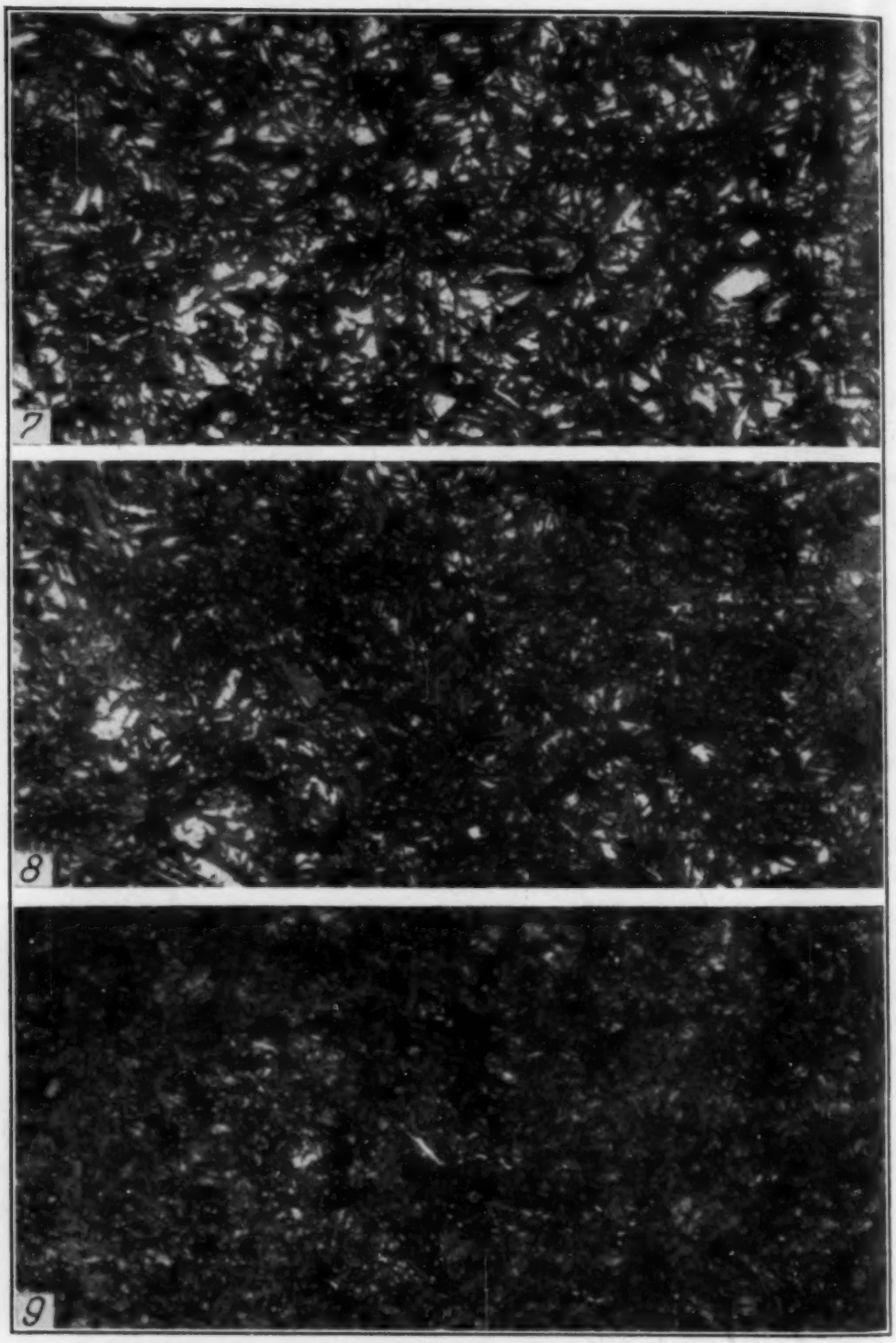

Fig. 7—Case Structure When Cooled to 1025 Degrees Fahr., Reheated to 1460 Degrees Fahr. and Quenched. Picral Etch. × 500.

Fig. 8—Case Structure When Cooled to 900 Degrees Fahr., Reheated to 1460 Degrees Fahr. and Quenched. Picral Etch. × 500.

Fig. 9—Case Structure When Cooled to 800 Degrees Fahr., Reheated to 1460 Degrees Fahr. and Quenched. Picral Etch. × 500.

the Ar′ range at the cooling rate under which the determinations were made.

Carpenter and Robinson[3] disagree with Bain and Davenport and state that if cooling stops, austenitic transformation stops and is therefore not isothermal. The present test offers no evidence in this respect since variations in holding time at the same temperature were not tried. It therefore cannot be said whether a longer hold at some higher temperature would be more or less effective than cooling to 900 degrees Fahr. (480 degrees Cent.) and holding a shorter time to make the total elapsed time equal. All that can be said is that at 900 degrees Fahr. (480 degrees Cent.), either because of temperature to which cooled or time held, the original austenitic grain structure was transformed. If the transformation is isothermal, as seems more probable, it is suggested that annealing cycles for 4815 and some heats of 4620 that are subject to formation of martensitic grains might be shortened by holding the steel at the nose or highest rate of transformation rather than allowing the temperature to drop.

General observations made by the writer show that in the case of any given steel the amount of austenite retained depends largely upon carbon content of the case, temperature from which quenched, and rate of cooling. S-curves do not indicate any effect of initial temperature, as such, from which cooling started. This would leave only the effect of excess carbide precipitation to account for the difference in amount of austenite between direct quenching from 1700 degrees Fahr. (925 degrees Cent.) and the delayed quench at 1460 degrees Fahr. (795 degrees Cent.). It appears rather doubtful if this is the entire explanation since the amount of excess carbide was very small and the austenitic zone was deeper than the observed depth of excess carbides. In the case of reheating to 1460 degrees Fahr. (795 degrees Cent.) the carbon content of the austenite should be the same in all remaining tests except for slight influence of diffusion. The finer grain size produced by transformation during cooling before reheating to 1460 degrees Fahr. (795 degrees Cent.) offers the most obvious reason for the differences in structures in those samples.

[3]H. Carpenter and J. M. Robinson, METAL PROGRESS, Vol. 37, 1940, p. 448.

Conclusion

Physical tests on the core as pseudo carburized and heat treated and on case hardened parts show that S.A.E. 4815 steel need not be cooled, after carburizing, to room temperature before reheating and quenching from 1460 degrees Fahr. (795 degrees Cent.) to obtain maximum physical properties in single treated parts.

Core properties were not very sensitive to the variations in heat treatments used but Izod results indicate that there is little or no advantage of cooling below 900 degrees Fahr. (480 degrees Cent.).

Impact properties of notched or unnotched case hardened Izod specimens depend chiefly on case depth, especially when core properties are similar, hence this test was not sensitive to case structures.

Bend tests as conducted proved to be the most sensitive to variations in case properties and showed a marked increase in case strength as cooling before reheating dropped from 1025 to 900 degrees Fahr. (550 to 480 degrees Cent.). This was accompanied by a distinctly finer-grained fracture in the case. The microscope reveals a corresponding but more gradual change in the amount of retained austenite and in the grain size and type of acicular structure.

It is believed the results confirm that transformation of austenite follows the pattern of the S-curve and the nose of the curve is between 1025 and 900 degrees Fahr. (550 and 480 degrees Cent.) in the steel investigated. Published Ar_1 points showing lower temperatures are believed to represent the end of Ar′ under the test conditions employed. These conclusions also suggest that annealing cycles might be shortened by holding at the nose of the S-curve followed by cooling as fast as desired rather than to let the temperature drop slowly until below the point given as Ar_1. Any desired distribution of free ferrite in hypoeutectoid steel must, of course, be controlled by cooling rates at higher temperatures.

From the results it may be predicted that high alloy steel whose cases most readily retain austenite on cooling and coarse-grained steels, or especially both, would be most susceptible to the observed changes responsible for the effect on the physical properties. The required cooling temperature and time held would depend on the location of the nose of the S-curve and transformation rate of the steel being tested. Excess carbide, if present in network form, would no doubt be an added factor affecting the properties.

DISCUSSION

Written Discussion: By John H. French, metallurgical department, White Motor Co., Cleveland.

This discussion will be limited to the structure and properties of the case of each tested sample, as it is in this area that the samples show significant changes when subjected to the various treatments.

The bend test affords the best chance to study the physical properties of the case of each sample. The results of this test, as tabulated, do not show the uniform variation that might be expected if the surface conditions were uniform in regard to disposition or presence of excess cementite. If cementite were uniformly in excess in the outer layer, you would expect a constant drop in the load at the first crack corresponding to the amount of lowering of the temperature before reheating, due to the sluggishness of the cementite going back into solution after once being precipitated. The results obtained indicate that the cementite distribution might not have been uniform. Not enough seems to have been said concerning the cementite. The bend test comparisons are hampered by lack of knowledge of the amount of this constituent in each piece. The first crack, for some samples, might have been due to localized cementite or to different amounts of the carbide in different samples. The results show varying case depths, but concentration as well as penetration of the carburized layer might very well have been presented.

It would be interesting to box-cool all of the samples from the carburizing temperature to room temperature and to examine the surface to establish more definitely the relative amounts of excess carbide present. Knowing more exactly the percentage of cementite in the case of each sample, the inconsistencies of the bend test might be blamed on varying compositions of different samples, or, if compositions proved to be uniform, the desultory results would have to be explained in other ways.

Not knowing the exact percentage of carbon in the case of each sample from the evidence presented, for further investigation of the bend test results a near eutectoid composition shall be assumed. In this way the effect of excess cementite becomes negligible. (McMullan establishes this condition as a fact in his treatise without, it seems, sufficient presented evidence of the case composition.)

The case fractures of the bend test specimens show a gradation from course for the direct quench samples (from 1700 degrees Fahr.), to fine, beginning with the samples cooled to 900 degrees Fahr. (480 degrees Cent.) from the carburizing temperature, reheated and quenched from 1460 degrees Fahr. (795 degrees Cent.). The purpose of box-cooling a carburized part to room temperature is to completely decompose the austenite, so as to establish a new (finer) austenitic grain size from the subsequent hardening temperature. The noted differences of the case fractures seems to be related to different degrees of austenitic decomposition.

As the temperature of the case is lowered in successive steps from the carburizing temperature, it is logical to assume that each decrease in temperature more nearly approaches the point of most rapid austenitic decomposition.

This point would be the nose (Ar') of the S-curve. (It would be interesting to know the length of time these samples were held at the various cooling temperatures, and to compare these times and temperatures with corresponding data obtained from an S-curve for this particular steel. It could then be shown definitely what temperature and time would be required for the most rapid and complete decomposition of the austenite.) If the above assumption is correct, the bend test, to which the case is most sensitive, should produce a definite relation between cooling temperatures and physical properties. Plotting pounds per square inch at first crack versus cooling temperatures and also deflection (inches) at first crack versus cooling temperatures, two curves are produced that strongly resemble the general pattern of an S-curve. (Plotting of pounds per square inch and deflection from right to left shows more clearly the similarity to an S-curve.) (Fig. 1A)

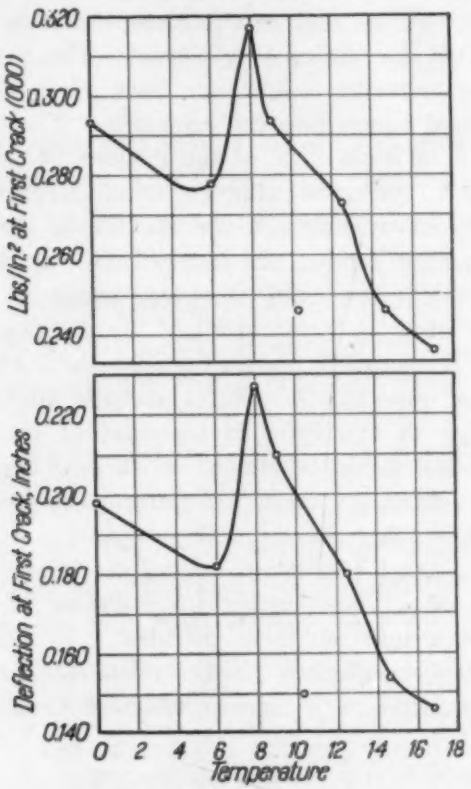

Fig. 1A

It will be noticed that the point corresponding to the 1025 degrees Fahr. (550 degrees Cent.) cooling temperature is excluded from the curves to show more clearly the S contour. It is difficult to explain the relapse of properties at this temperature. The BHN of the core of each sample is also far below average, which complicates any explanatory attempts. The question of excess cementite in the case can sensibly be raised here. No discussion of this range is presented by McMullan. The answer should prove interesting. The substantial increase in physicals of the 900 degrees Fahr. (480 degrees Cent.) sample seems substantiated by a noticeably finer martensitic structure as compared with samples not cooled to as low a temperature before hardening.

Again in this case the amount of excess cementite should be more conclusively known. However tracing the curves, excluding both extreme physicals, the pattern of a less pronounced S-curve can be seen.

If the S-curve theory is well founded, there should be evidence of both coarse and fine martensite in the hardened case. Some untransformed austenite would cause a coarse martensite, while the decomposed solid solution when reformed at the hardening temperature would establish a finer quenched structure. If this difference in strucutre could be shown, it would further fortify the S-curve theory. McMullan states that his results follow the pattern of the S-curve in regard to the transformation of austenite and establishes the nose of the curve between 900 and 1025 degrees Fahr. (480 and 550 degrees Cent.). The curves presented here establish the nose of the curve or Ar′ nearer to 800 degrees Fahr. (425 degrees Cent.). McMullan's mere statement of a relation between results and the S-curve is not supported in his paper by any pointed discussion of facts or figures.

It has been the point of this discussion to suggest an oversight in experimental procedure by McMullan on one hand, and to attempt to substantiate more fully than does his paper one of his most important conclusions.

Box-cooling representative samples for each case hardened group and examining for excess cementite in the outer surface might have added useful data to the experimental evidence.

The evidence presented in support of the S-curve theory is believed to be sound. Other conditions remaining uniform, there should be a definite S-curve relation between physical properties and cooling temperatures. Such an established relationship would be a prime requisite for practically effecting McMullan's plan. Although there is no evidence to support the idea of a coarse and a fine structure simultaneously present in the hardened case, experimental work should prove this true.

Written Discussion: By R. J. Peters, metallurgical department, Warner Gear Division, Borg-Warner Corp., Muncie, Ind.

The author's paper brings out a very useful application of isothermal transformation contributing to better control of case quality and improved economy of production.

The presence of excessive retained austenite on the surface or in the hyper zone is not desirable. The treatment proposed should materially improve wear resistance.

The writer can testify to the value of the author's conclusions regarding the benefit of this procedure in annealing. We have used this cycle for sometime for annealing 4815, 2512 and 4620 to prevent the occurrence of martensite with complete satisfaction. When martensite occurs, however, it has been found necessary on re-annealing to reheat to 1650 degrees Fahr. (900 degrees Cent.) or over and then drop to 800 to 1000 degrees Fahr. (425 to 540 degrees Cent.) and hold. The work may then be pulled or, on a continuous cycle, pushed out at that temperature.

One thing which would be of considerable interest is the effect of this treatment on dimensional changes. Anything contributing to greater uniformity or better stabilization of the case and core should materially affect movement.

Written Discussion: By Howard Scott and John L. Fisher, Westinghouse Electric & Manufacturing Co., E. Pittsburgh, Pa.

One of the misconceptions that have retarded the progress of physical metallurgy is the widely held opinion that ductility of the core contributes to the toughness of a case hardened steel. Mr. McMullan very effectively exposes this fallacy by showing that cracks appear in the case before the core ruptures. Since cracking of the case constitutes failure and the core cannot absorb the plastic deformation implied by "toughness" until the case cracks, core toughness contributes nothing to the prevention of failure. Moreover, the strength of case hardened steel is mediocre as compared with homogeneously hardened steels as we shall demonstrate presently.

The foregoing remarks are not intended to imply, however, that some advantage does not or cannot accrue from a soft core. The only implication intended is that any benefit conferred by a soft core is derived from some other property than ductility. A significant property in this connection is density, the core being more dense than the high carbon case after hardening. Because of this difference in density the case is under high compressional stress unless tempered considerably under 60 R_c. Initial compression at the surface favors resistance to bending because ultimate strength in this high hardness range is much greater in compression than in tension so there is no danger of failure under compressive stress. On the tension side, too, conditions are favorable to a high ultimate tensile strength because the initial compression must be relieved before tensile stress develops there. One would expect therefore that surface hardened steels with a soft core would have higher strength in bending than homogeneously hardened steel of comparable composition. Experiments on carburized steels, however, do not verify this expectation, presumably because there are other adverse factors present.

Seeking information on the strength of carburized steels, we also used a bend test. It is a highly significant test for steels of surface hardness over 55 R_c because service loading is usually by bending and bending strength correlates well with tensile strength though the observed values are much higher. Being also a simple and inexpensive test to make, we have used it extensively on tool as well as carburized steels. The essential difference between our test and Mr. McMullan's is in the size of the test specimen used, our specimen being ¼ by ⅜ inch with a 2-inch span between roller supports.

Tests made with the smaller specimen on gas carburized S.A.E. 2512 steel supported quantitatively certain of the author's conclusions and as well demonstrated the inferior strength of this carburized steel relative to a homogeneously hardened tool steel. Case depth on the test specimens was 0.060 to 0.070 inch. They were carburized all over at 1700 degrees Fahr. (925 degrees Cent.) and cooled, possibly, but not necessarily, to room temperature before reheating and quenching in oil from 1500 degrees Fahr. (815 degrees Cent.) at another plant. Tests were made after tempering to surface hardness values from 50 to 66 R_c with the bending strength plotted against hardness in Fig. 2A where each point represents a single observation.

Considering the observations plotted first without regard to any classification, it is seen that there is a wide scatter among them, much wider than for

fully hardened tool steels. Accordingly, a search was made for factors that might be responsible for a major part of the scatter. Examining the fractures first, many were found to be distinctly coarse-grained; so a distinction was made on this basis. As expected, the fine-grained specimens were consistently stronger than the coarse-grained ones, Fig. 2A. The reason for the grain size difference under presumably identical hardening practice, however, is still obscure.

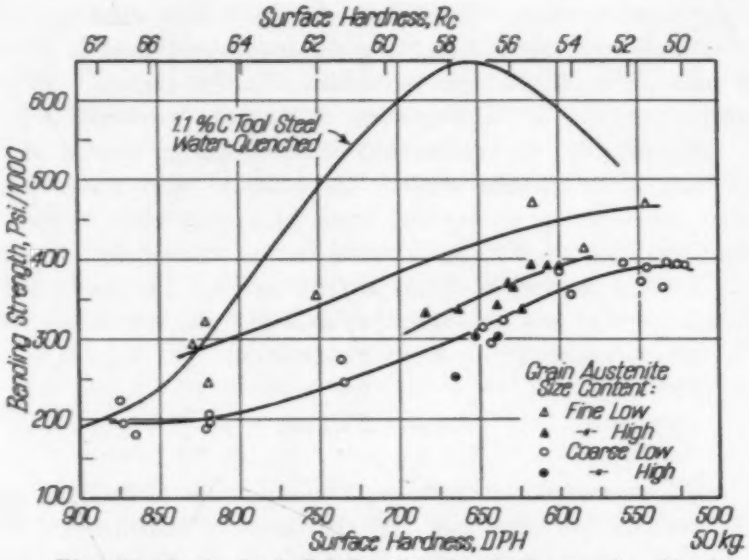
Surface Hardness, Rc
67 66 64 62 60 58 56 54 52 50
1.1 % C Tool Steel Water-Quenched
Bending Strength, Psi/1000
600 500 400 300 200 100
Grain Austenite Size Content:
Fine Low
High
Coarse Low
High
900 850 800 750 700 650 600 550 500
Surface Hardness, DPH
50 kg.

Fig. 2A—Carburized S.A.E. 2512 Steel Compared with 1.1 Per Cent Carbon Tool Steel.

Though the preceding classification reduced materially the scatter of observations in each category, sufficient scatter remained to suspect still another unidentified variable affecting strength. Observations on tool steels had disclosed that bending strength at a particular hardness diminishes with austenite content so evidence of differences in austenite content was sought. The test used for austenite content was the hardness change produced by cooling the broken test specimens in dry ice (—80 degrees Cent.) for 1 hour. They either increased in hardness by 130 to 200 points DPH (at least 5 points R_c) or changed less than 30 points DPH. Accordingly, the former were designated high austenite content and the latter low austenite content in Fig. 2A. Later it was learned that those identified as low in austenite content had either been cooled in dry ice before tempering or tempered at or above 500 degrees Fahr. (260 degrees Cent.).

The discordance between the original observations is now completely resolved, the specimens falling into four groups with respect to relative bending strength at the same hardness, namely:

(1) Fine grain size—low austenite content
(2) Fine grain size—high austenite content
(3) Coarse grain size—low austenite content
(4) Coarse grain size—high austenite content

There are only 3 specimens in group (4), but every one falls below the curve for group (3) so their position is hardly accidental. Each of the other

groups is represented by a mean curve in Fig. 2A which is established by no less than 7 observations. The spread between the top and bottom curves is so wide as to justify great effort in the control of carburizing practice so as to obtain consistently both a fine grain size and low austenite content. Practical means for doing so are being sought in our Laboratories.

The highest bending strength recorded for case hardened S.A.E. 2512 steel is still far short of that obtained in homogeneously hardened carbon tool steel over the hardness range 54-63 R_c. At the widely used surface hardness of 60 R_c, the highest value expected for the carburized steel is 380,000 pounds per square inch while 580,000 can be obtained in the carbon tool steel having the same carbon content as the maximum in the case hardened steel. There is no obvious reason why the carburized steel properly treated should be so inferior, in fact, a substantial reason has already been given for expecting even superior strength in carburized steel of comparable composition. We believe, therefore, that it will be possible to improve materially the bending strength and related properties of carburized steels if the remaining factor or factors responsible for low strength be isolated. A search for the missing factor or factors is underway in our Laboratories.

Author's Reply

Mr. French expressed the opinion in his discussion that not enough had been said concerning the cementite and that lack of uniform variation might be due to uneven distribution of that constituent. In the paper it was stated that the time of cooling from 1700 to 1460 degrees Fahr. (925 to 795 degrees Cent.) was more than 3 hours and a similar time elapsed between 1460 and 1250 degrees Fahr. (795 and 675 degrees Cent.). Had the carbon been high enough to produce amounts of excess cementite sufficient to have a material effect on the properties, most of the cementite would have been precipitated by the slow cooling to 1250 degrees Fahr. (675 degrees Cent.). The amount precipitated below 1250 degrees Fahr. (675 degrees Cent.) should be negligible, if any, and the writer doubts that a constant drop in the load should be expected, regardless of carbon content of the case, corresponding to the amount of further lowering of the temperature before reheating. Even granting such a possibility, the observable evidence indicates that cementite could have had but a very minor influence for two reasons. The first is that only small amounts of cementite were visible in any of the specimens and those particles were quite well scattered and more or less completely spheroidized. Fig. 9 shows the typical distribution of cementite in all the reheated specimens. No carbide particle much larger than that near the center of Fig. 9 was observed and none existed in a network form. The second reason is that, as mentioned in the paper, diffusion and decarburization during reheating produced a surface zone with entire absence of visible excess cementite. In the absence of any apparent pronounced weakness farther in, it is assumed that the crack started in the highest stressed, excess carbide free, zone at the surface.

It is believed that box cooling as suggested would not be of benefit and might be misleading. Distribution of constituents may be of much more im-

portance than the actual amounts present. Box cooling would produce a different distribution of cementite than that present in the heat treated samples. The author believes the evidence warrants Mr. French's assumption of near eutectoid composition for the remainder of his discussion. It is believed that the variations that did occur were caused by surface imperfections, uneven case depth, effect of the copper plate on the case at the corners, etc. The effect of some of these variables could have been reduced by a larger number of tests to average the inequalities, or by more carefully prepared specimens, etc., but the purpose of the investigation did not justify the time and expense.

Time of holding samples at 1460 degrees Fahr. (795 degrees Cent.) and at 1250 degrees Fahr. (675 degrees Cent.) while still in the compound is not known exactly but believed to be from ½ to 1 hour. In all other cases time of cooling to each successively lower temperature was ½ hour and holding time was ½ hour.

The stress-temperature and deflection-temperature curves plotted by Mr. French from the data in the paper are interesting but it is believed that it is merely a matter of chance that they resemble complete S curves. It is reasonable to believe that the curve might follow the contour of an S curve from the start of austenite decomposition down to the temperature of the nose. Considering the manner in which the tests were conducted, there is no reason for the lower part of the curve to follow an S curve pattern. Since samples cooled to each successively lower temperature also passed through all the cycles of the samples removed from the furnace previously, each lower temperature represented an additional, not an entirely separate treatment. For example, the samples cooled and held at 600 degrees Fahr. (315 degrees Cent.), also were held at 1025, 900 and 800 degrees Fahr. (550, 480 and 425 degrees Cent.) before cooling to 600 degrees Fahr. (315 degrees Cent.). The austenite in 600 degrees Fahr. (315 degrees Cent.) samples therefore should be equally, if not more fully decomposed, than those at 800 and 900 degrees Fahr. (425 and 480 degrees Cent.), rather than less as in the S curve pattern. The inflection point at 800 degrees Fahr. (425 degrees Cent.) more probably resulted from some of the variables mentioned above. The weight of evidence indicates the nose of the curve to lie between 1025 and 900 degrees Fahr. (550 and 480 degrees Cent.).

An examination of Figs. 7 and 8 will show the presence of a coarse and fine structure simultaneously present in the hardened case.

Mr. Peters' remarks on annealing offer interesting information on the effectiveness of isothermal annealing treatments on carburizing steels subject to formation of martensitic grains.

Messrs. Scott and Fisher have presented data that are valuable additions to the information on the strength of case hardened steels and it is hoped they will be successful in their attempt to find the cause for lower bending strength than obtained with steels of uniform carbon content which likewise has been observed by the author. (Reference 1 in the paper).

It should be pointed out that conclusions arrived at from bend tests may depend on sample size and case depth. The specimens used by Messrs. Scott and Fisher were only ¼ inch thick and the case depth 0.060 to 0.070 inch.

The maximum stress in the core could therefore be no more than half the maximum at the surface of the case, consequently core properties would have no bearing on the results. Thicker specimens or thinner case depths permitting higher stresses in the core may permit yielding of the core immediately below the case. Under such circumstances core properties may become important.

The discussers' Fig. 2A requires a few comments. They state "The reason for the grain size difference under presumably identical hardening practice, however, is still obscure". Previously they had mentioned that specimens were cooled, possibly, but not necessarily, to room temperature before reheating and quenching. As pointed out in the author's paper, variations in that cooling temperature could cause not only differences in grain size, but in amount of austenite present also. Classification of the specimens in groups in Fig. 2A is an interesting one and confirms work previously reported by the author on the effect of both grain size and the amount of austenite. (Reference 1 in the paper). How much of the increase in strength is due to elimination of austenite and how much to removal of internal stresses would be difficult to determine. Note that in all cases of Fig. 2A, regardless of grain size or austenite content, the strength drops as hardness increases which is contrary to expectations in the absence of high internal stresses.

It should be kept in mind that maximum bending strength is not always the most important factor to be considered in case hardened steels. For example, under conditions of elevated operating temperatures, such as results from friction between parts poorly lubricated, the presence of some austenite may be an aid in preventing wear and scuffing of gear teeth.

The author is pleased to note that others agree that the bend test is a very suitable one for studying properties of case hardened steels and wishes to thank those taking part in the discussion for calling attention to points not clearly covered in the paper and for presenting confirming or additional information. It is hoped that the points of disagreement will lead to further work to determine which is correct.

THE RATE OF FORMATION OF TIN-IRON ALLOY DURING HOT DIP TINNING AS MEASURED BY A MAGNETIC METHOD

By Alan U. Seybolt

Abstract

By the use of a magnetic method it was found possible to follow the course of the formation of the tin-iron alloy (mostly $FeSn_2$) during the hot dip tinning of samples of tin can stock. The method depends upon the conversion of the ferromagnetic iron to nonferromagnetic $FeSn_2$.

The relation $d = At^{\frac{1}{2}}$ was found to hold in the temperature range of 500 to 625 degrees Fahr., where d is the amount of iron or tin reacting to form $FeSn_2$, A is a constant at a stated temperature, and t is time. Also, the constant A, which can be considered the amount of $FeSn_2$ formed in unit time, varies with temperature according to the expression $A = Be^{-\frac{Q}{RT}}$ where B is a constant, and e, Q, R and T have the usual significance.

IT is well known that the compound $FeSn_2$ is formed at the steel-tin interface during the manufacture of tin plate by the hot dipping process. At least three investigations (1), (2), (3)[1] have confirmed the existence of this compound, next to pure tin, as the most tin-rich phase in the iron-tin system. Furthermore, it is well established that the compound $FeSn_2$ is the only one formed in appreciable amounts during the hot tinning of steel.

While these qualitative aspects of the formation of $FeSn_2$ have been clear for some time, the literature reveals very little on the quantitative nature of its formation. The rate of formation of $FeSn_2$ on mild steel was therefore studied as a function of time and temperature.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. The author, Alan U. Seybolt, is associated with the Battelle Memorial Institute, Columbus, Ohio. Manuscript received June 25, 1941.

Method of Estimating the Amount of $FeSn_2$ Formed

After some preliminary experiments with orthodox chemical stripping methods which depend upon selective solution of the tin and the $FeSn_2$ "alloy layer", this method was discarded because of its slowness and inaccuracy. It was evident that to obtain satisfactory measurements of the thickness of the alloy layer, it must be measured in place rather than depending upon stripping methods. Microscopic examination was considered but rejected because it is time consuming and because the alloy layer ($FeSn_2$) is very irregular and hence not susceptible to accurate measurement.

A magnetic method which had the advantage of both speed and adequate accuracy was developed and used throughout the investigation. Samples of tin can stock, 0.75 by 3 inches, were inserted in a search coil which was connected in opposition to a duplicate search coil containing a similar, but untinned, specimen. The search coils were placed inside a 30-inch solenoid of 1-inch bore, about 10 inches from either end. The two free leads from the search coils were connected, through a suitable electrical system, to a ballistic galvanometer. A direct current of 2 amperes was passed through the solenoid, and when this current was reversed, induced currents were set up in the search coils. Since the two identical search coils were in opposition, the induced currents in the search coils balanced each other if the two specimens were of equal dimensions. However, if one of the specimens were placed in a tin bath, and some of the iron became converted to $FeSn_2$, the induced currents no longer balanced, and a certain deflection was observed in the galvanometer. $FeSn_2$ was found by experiment to be nonferromagnetic. The deflections read on the galvanometer scale were consequently a function of the amount of ferromagnetic iron removed or the amount of $FeSn_2$ formed. It was a simple matter to calibrate the instrument so that deflections could be converted to thickness of iron removed in inches. To check the magnetic method, some tests were performed by etching away the iron with nitric acid and weighing the strips after successive etches. It was found that the weight loss determined by the magnetic method was about 14 per cent low compared to the direct method. However, since this discrepancy appeared to be quite constant for various etching times, the method was considered satisfactory as it apparently yielded results sufficiently consistent and of the right order of magnitude.

Description of the Apparatus

Fig. 1 shows the circuit used in making the magnetic tests. The central reversing switch marked "test" and "standardizing" was used in the test position when making measurements on the tinned samples.

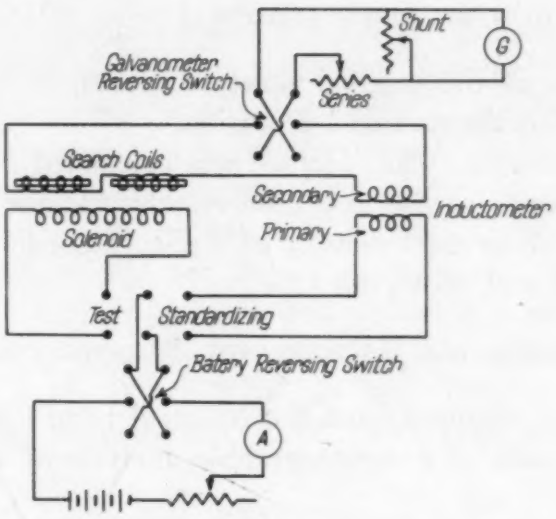

Fig. 1—Description of the Circuit Used. G—Leeds and Northrup Type R Ballistic Galvanometer. Shunt—Decade Resistance 1-9999 Ohms. Series—Decade Resistance 1-999 Ohms. Search Coils—Two Flat Coils ⅛ x ⅜ x 1½ Inches. 1¼ Inches of No. 36 Enamel-Covered Wire. Solenoid—1 Inch Bore—30 Inches Long. Field Strength, Oersteds = 49.5 I. Inductometer—Brookes 0-12 Milli-Henrys. A—Ammeter.

When measuring the amount of iron converted to $FeSn_2$, the series resistance was zero while the shunt resistance was set at 9000 ohms for maximum sensitivity. A somewhat higher shunt resistance could have been used, but no measurable increase in sensitivity would have resulted. Ordinarily 30 volts were applied to the solenoid and the battery resistance was set to give 2 amperes. The secondary of the mutual inductance was always in series with the search coils so that no adjustment in this part of the circuit was necessary when measuring the standard deflection. The standard deflection was that which would have occurred if all the iron in the test sample had been transformed to nonferromagnetic material, namely, $FeSn_2$. This deflection was always very large compared to the maximum deflection which would be measured directly. In order to obtain this standard deflection, the test sample was removed

from its search coil. By the use of the mutual inductance (inductometer) it was possible to decrease the sensitivity of the galvanometer and obtain deflections within the galvanometer scale, and then recalculate back to the deflection which would have occurred with full sensitivity.

The thickness of the iron removed from one side of the sample, d, was calculated by the simple relation $d = \frac{m}{2S}(0.010)$ where 0.010 is the thickness of the original sheet in inches, m is the measured deflection and S is the standard deflection.

The thickness of $FeSn_2$ formed was calculated merely by multiplying the thickness of the iron removed by a factor of 4.83, calculated from the theoretical density of $FeSn_2$ according to the X-ray results of Ehret and Westgren (2).

Materials Used in the Investigation

The tin was obtained from the National Lead Company. Table I shows the results of a spectrographic analysis of this material.

Table I
Spectrographic Analysis of the Tin

Pb	0.15 Per Cent
Bi	0.04
Cu	0.03
Sb	0.08
As	0.02
Fe	0.004
Ni	0.002
Co	tr
Ag	1.5 ounces per ton
In	0.01

The steel was normal can stock, 0.010 inch thick, and had the following analysis:

Carbon	Manganese	Sulphur	Phosphorus	Silicon
0.07	0.34	0.075	0.020	0.004

Experimental Procedure

The tin was contained in a clay-graphite crucible with a cover of molten zinc chloride. About 5 pounds of tin were used, which provided a depth of about 4 inches. The crucible was situated in an electric pot furnace and the temperature controlled to within ± 5 degrees Fahr. by a potentiometric controller. Before im-

mersing the strips into the tin bath, they were customarily annealed for periods of time ranging from ½ hour to 3 hours at a temperature equal to, or somewhat higher than, the tin bath temperature. However, no direct correlation could be found between this heat treatment and the tinning which followed. In general, more consistent results were obtained with the annealing treatment than without it.

The specimens were pickled for a few minutes in 1:1 hydrochloric acid to remove surface scale and foreign materials. One sample was placed in the "standard search coil" and left there during the course of measurements on similar tinned specimens. A sample to be tinned was pickled, cleaned, dried, and then measured in the magnetic tester to obtain the initial deflection. Then it was removed and placed in the pickle for a few seconds and, while still wet, immersed in the tin. In general, the following schedule of tinning periods was used for each specimen: 5 min., 10 min., 15 min., 30 min., 1 hr., 2 hr., 4 hr., 8 hr., 24 hr. The tin bath was held at the following temperatures: 500, 550, 600, and 625 degrees Fahr.

Results

The first experiments were made at 625 degrees Fahr. (330 degrees Cent.), which is approximately the temperature used in commercial tinning. The thickness of iron removed by conversion to $FeSn_2$ at various periods of time was at first plotted on semi-log paper to shorten the time scale. It was observed that the data fell on a smooth curve, concave upwards. This appeared to indicate that the data were obeying some simple law. It appeared likely that the law which Pilling and Bedworth (4) found for the growth of oxide films on metals would apply here because the growth of $FeSn_2$ from the liquid tin should be very similar to the growth of an oxide film from the surrounding oxygen atmosphere. This simple relationship may be expressed as $d = At^{1/2}$, where d is the amount of iron (or tin) reacting to form $FeSn_2$, t is time, and A is a constant for a stated temperature. The amount of iron reacting to form $FeSn_2$ is obviously directly proportional to the actual amount of $FeSn_2$ formed. Hence, if this law applies, the data should fall on a straight line if the logarithm of d is plotted against the logarithm of t because $\log d = \log A + \frac{1}{2} \log t$. Log A is the intercept on the d axis for unit time and the slope of the line is ½. When the

data for 625 degrees Fahr. (330 degrees Cent.) were plotted on log-log paper, a straight line was produced, as seen in Fig. 2. The actual empirical equation was found to be $d = 0.000021t^{.495}$, where 0.000021 is the thickness of $FeSn_2$ (4.83 times the thickness of iron

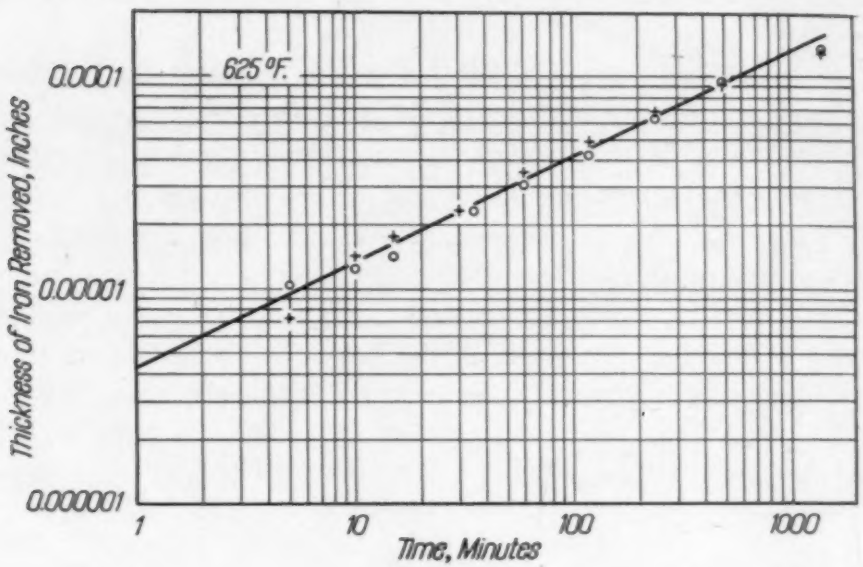

Fig. 2—Thickness of Iron Converted to $FeSn_2$ at 625 Degrees Fahr. on Tin Can Stock After Various Time Intervals.

removed) in inches formed on one side of the steel at the end of 1 minute. This value was obtained by extrapolation, as no data were plotted for immersion times less than 5 minutes. It was found that the reproducibility of the readings was not satisfactory for very short periods of immersion, but for periods of 10 minutes or over, the reproducibility was generally quite satisfactory as seen from the two sets of data plotted in Fig. 2.

Similar results were obtained for different tinning temperatures, except that in the case of the data at 500 degrees Fahr. (260 degrees Cent.) the readings for periods up to about 30 minutes had a peculiar tendency to remain constant instead of increasing in a normal fashion. Three different specimens at this temperature all showed the same effect. In drawing the straight line in Fig. 3, the data obtained for the first 15 minutes were neglected. Figs. 4 and 5 show similar data plotted for 550 and 600 degrees Fahr. (290 and 315 degrees Cent.), respectively.

In Table II are given a summary of the A values and slopes.

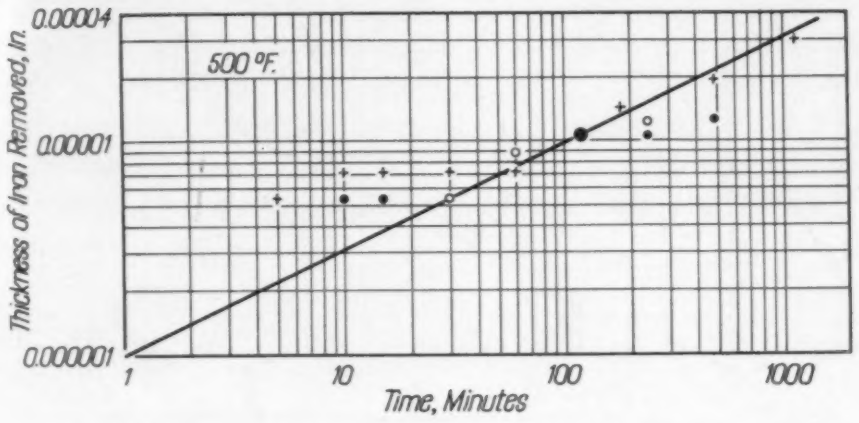

Fig. 3—Thickness of Iron Converted to $FeSn_2$ at 500 Degrees Fahr. on Tin Can Stock After Various Time Intervals.

Table II
Values of A and Slopes Obtained at the Four Investigated Temperatures

Temperature Degrees Fahr.	A (Thickness of $FeSn_2$ Formed in 1 Min. in Inches)	Slope of Log d vs. Log t
625	21×10^{-6}	0.495
600	15×10^{-6}	0.505
550	8.2×10^{-6}	0.495
500	4.8×10^{-6}	0.500

Rate of Formation of $FeSn_2$ as a Function of Temperature

Since the constant A (thickness of $FeSn_2$ formed in 1 minute) is a rate constant in the diffusion process it must depend upon the temperature according to the equation $A = Be^{\frac{-Q}{RT}}$ which expresses the relationship between a diffusion constant and temperature. In this equation,

e is the base of natural logarithms
Q is a heat of activation
R is the gas constant
T is the absolute temperature
B is a constant

Fig. 6 shows the result of plotting A directly on a logarithmic scale against $\frac{1}{T}$. A straight line results since $\log A = \log B - \frac{Q}{R}\left(\frac{1}{T}\right)$. Q is found to be 14,300 calories per mol.

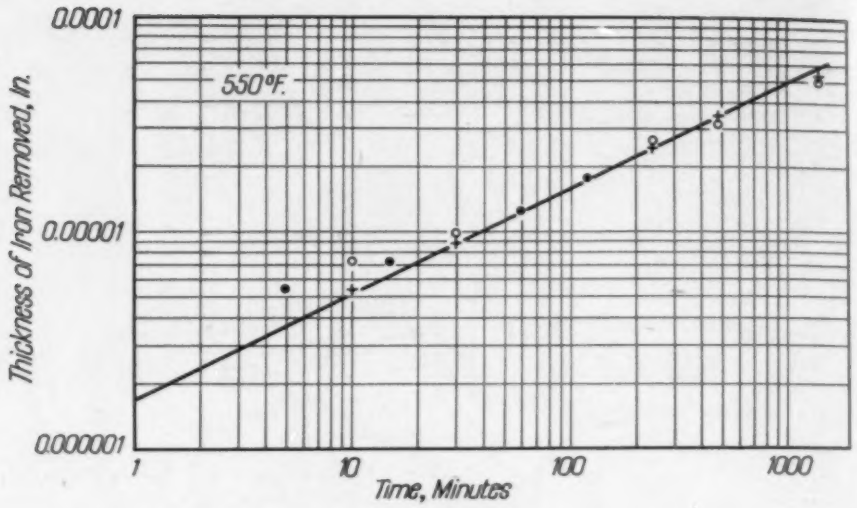

Fig. 4—Thickness of Iron Converted to $FeSn_2$ at 550 Degrees Fahr. on Tin Can Stock After Various Time Intervals.

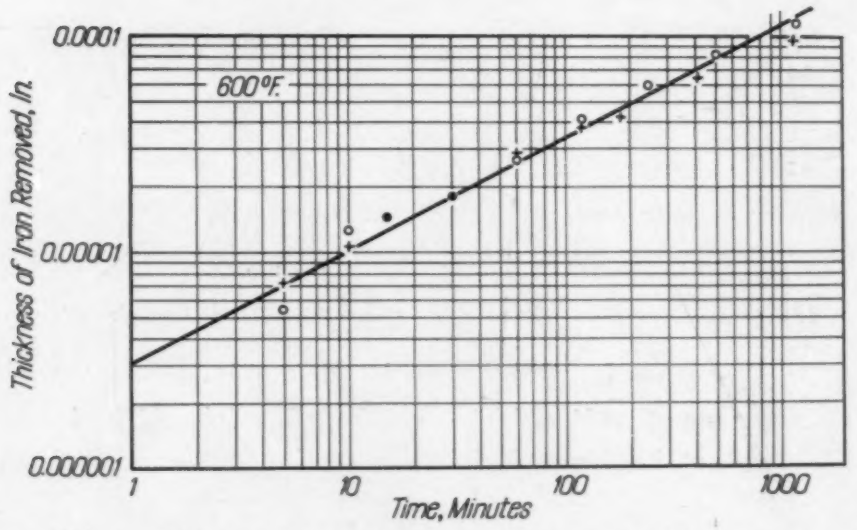

Fig. 5—Thickness of Iron Converted to $FeSn_2$ at 600 Degrees Fahr. on Tin Can Stock After Various Time Intervals.

Discussion

$FeSn_2$ has been found to form on tinning steel in a manner quite analogous to the formation of an oxide film on metals. The constant A has been found to behave like a diffusion constant. No claim to absolute accuracy is made in regard to the thickness of $FeSn_2$ formed, but the figures obtained are probably of the right order of magnitude.

The magnetic method has the disadvantage of being an indirect method, as it measures the amount of iron removed rather than the amount of $FeSn_2$ formed. Further, although the amount of iron removed must be directly related to the amount of $FeSn_2$ formed, the measurements at best can only indicate the total amount of $FeSn_2$ formed, hence not necessarily the amount of $FeSn_2$ on the steel. Since

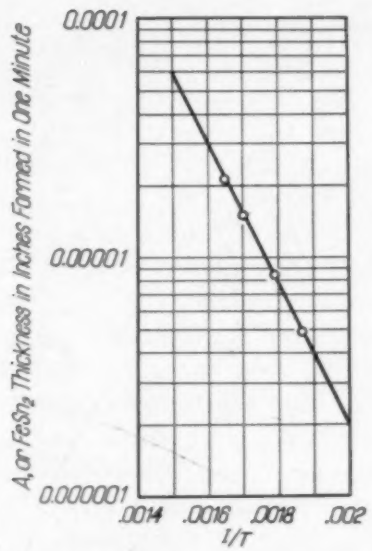

Fig. 6—"A" Plotted on Logarithmic Scale Against the Reciprocal of the Absolute Temperature.

the quantity measured was the amount of iron removed from the test samples, the data were plotted as thickness of iron removed rather than thickness of $FeSn_2$ formed. However, in discussing the results, it seemed more direct to refer to $FeSn_2$ formed under various conditions. The rate of $FeSn_2$ formation in commercial hot dipping would be expected to be more rapid because of the disturbance of the tinned surface as it passes through the tin pot.

In summarizing, the magnetic method has much to recommend it for studies in tinning, galvanizing, or similar processes in which it is desired to investigate the rate of dissolution of steel in the coating bath. It is not well adapted to use as a routine tool for the determination of alloy coating thicknesses.

It is a pleasure to acknowledge the assistance of members of the Battelle staff in planning this investigation, and thanks are extended to the International Tin Development and Research Council for permission to publish this paper.

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DISCUSSION

Written Discussion: By H. S. Van Vleet, metallurgical engineer, American Can Co., Maywood, Ill.

The author is to be congratulated for his contribution to knowledge regarding the rate of tin-iron alloy formation during the hot tinning of sheet steel.

The correlation of time and temperature is, apparently, closely related to the rate of formation of an oxide film on metals. In the manufacture of tin plate the time of exposure of the steel sheets to the molten tin rarely exceeds a time interval longer than 7 to 10 seconds and almost never exceeds 30 seconds, even on menders which are given successive passes through the tinning operation. It would be interesting to extend these studies to include those exposure times employed in commercial tinning practice.

Steels normally applied in tin plate manufacture in this country carry a sulphur content from 0.020 to a maximum of 0.050. Also, tin from the straits settlements of high purity is generally used for the production of tin plate for food containers. It would, therefore, be of considerable value to the tin plate industry if the author could in future work study the rate of tin-iron alloy formation on this type of tin plate under conditions of tinning time very closely representative of those existing in the commercial manufacture of tin plate.

Written Discussion: By D. H. Rowland, senior metallurgist, Research Laboratory, Carnegie-Illinois Steel Corp., Pittsburgh.

Dr. Seybolt is to be complimented on the development of a new and rather ingenious method for determining the rate at which iron and tin alloy in molten tin.

Although not available in the literature, a considerable amount of information has been accumulated by the tin plate industry concerning the behavior and growth of the iron-tin alloy on tin plate. It is known, for example, that all of the iron-tin alloy formed does not necessarily remain on the steel surface when sheet steel specimens are held in molten tin for extended intervals of time. In general, for a given steel, the amount of alloy which dissociates itself from the steel at 600 degrees Fahr. in a given length of time will be greater than the amount which will come off in the same length of time at, say, 550 degrees Fahr. (285 degrees Cent.). For this reason the information presented by Dr. Seybolt, which represents the total amount of alloy formed, was particularly welcome because it made possible a comparison with similar

data obtained by means of metallographic measurements, which represent the amount or thickness of the alloy actually on the steel surface.

In comparing these data, it was found that the magnetic and metallographic curves practically coincided for a temperature of 500 degrees Fahr. (260 degrees Cent.), but, as the temperature increased, the slopes of Dr. Seybolt's curves became progressively steeper than those obtained by microscopic measurements.

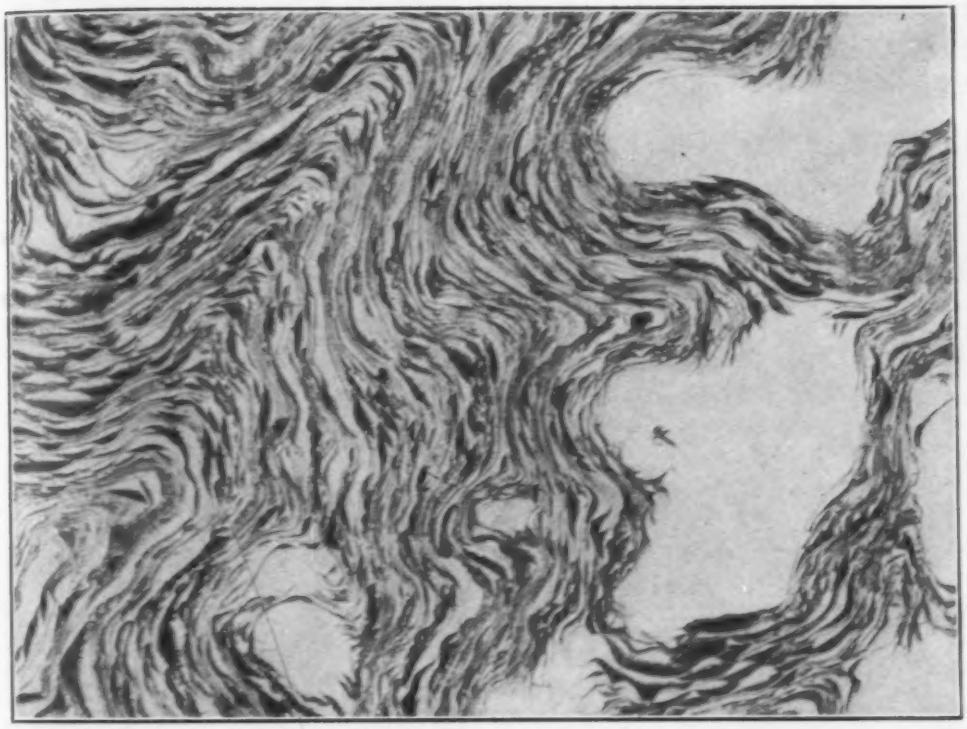

Fig. 1A—Flux Pattern on Steel Base of Tin Plate After Removal of Tin and Iron-Tin Alloy. × 2.5.

It seems probable, that had the same steel and tin been employed in the two investigations, the amount of alloy which dissociated itself from the steel would have been proportional to the difference in the slopes of the two sets of curves for the various temperatures.

The successful preparation of tin plate specimens for metallographic examination is largely a matter of technique, and once that technique is mastered the polishing and etching of cross sections requires very little more time than ordinary sheet steel specimens of similar gage.

It is admitted that the alloy layer is seldom if ever smooth, nevertheless the microscope is quite capable of giving results of the right order of magnitude when a magnification of 500 diameters is employed. This is particularly true if the iron-tin alloy has been allowed to form on sheet steel surfaces with a finish comparable to that commonly obtained in present day tin plate practice. Measurements have been readily obtained on sheet steel specimens which were held in molten tin at temperatures up to 600 degrees Fahr. (315 degrees Cent.) for periods of time up to 10 hours. For a temperature of 625 degrees Fahr.

(330 degrees Cent.), however, microscopic measurements do become increasingly difficult as the time of immersion is prolonged.

It seems possible that several factors may influence the rate of formation and smoothness of the alloy, such as grade of steel, heat treatment and surface condition prior to tinning or fluxing. Certainly the surface finish of the steel base markedly influences the smoothness of the alloy layer. This is exemplified even on commercial tin plate produced by the cold reduction process, a plate having a very smooth surface finish. The differential etch produced by the flux, although microscopic in character, is sufficient to cause surface irregularities in the alloy, not because of differences in the average thickness of the alloy but because of the manner in which the alloy builds up in these areas.

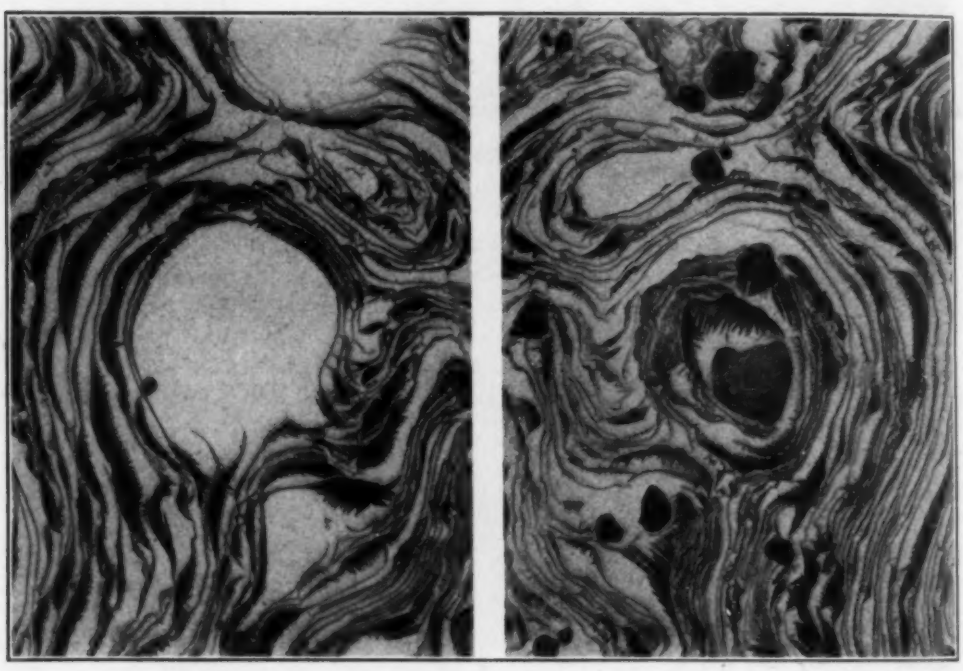

Fig. 2A—Flux Pattern on Surface of Tin Plate After Removal of Tin Coating Only—Oblique Illumination. × 8. Left—One side of Tin Plate. Right—Opposite Side Same Area.

This point is best illustrated by showing three photographs. It should be mentioned that the flux pattern shown in these photographs is revealed when the tin portion of the coating is removed.

The photograph, Fig. 1A, shows the surface of the steel base after removal of the coating on commercial hot-dipped tin plate. The pattern of alternate dark and light areas is characteristic, but the distribution and arrangement of these areas appear to be dependent to a large extent on the ebullition in the flux and the speed at which the plate passes through the flux. Whatever the distribution and arrangement may be, however, the pattern observed on one side of the sheet tends to be a negative of that on the opposite side, that is, dark and light areas on one side of the sheet are usually reversed on the opposite side. This is illustrated in Fig. 2A.

If sheet steel is passed slowly through a relatively quiet flux, swirls are almost entirely absent after removal of the coating; the dark and light areas

assume a more uniform spacing and become more or less parallel to the surface of the tin bath. On the other hand, numerous swirls and irregular spacing occur if the plate is passed quickly through an actively bubbling flux.

Microscopic examination of the pattern at high magnification reveals that the dark areas are not as rough as the light, indicating that the flux differentially etches the steel surface. This circumstance would seem to satisfactorily explain why the pattern observed on any particular area of the steel surface is substantially duplicated on the surface of the iron-tin alloy layer in the same area, as in Fig. 2A. Obviously, the surface contour of an alloy layer as thin as that on commercial hot-dipped tin plate, seldom more than 20 to 25 millionths of an inch thick, would be markedly influenced by the nature of the

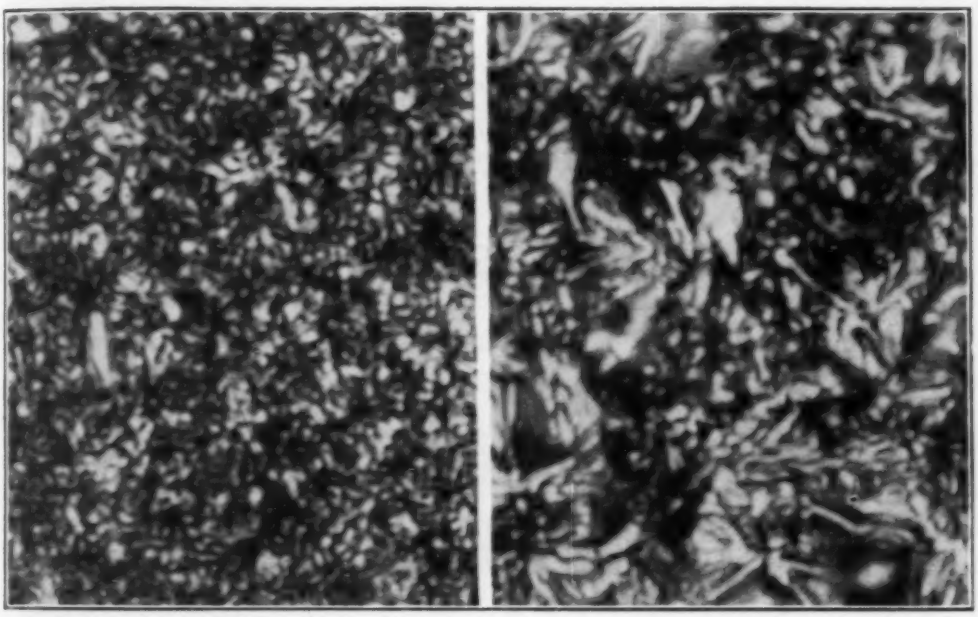

Fig. 3A—Surface of Iron-Tin Alloy on Tin Plate After Removal of Tin Coating Only—Vertical Illumination. × 3000. Left—Dark Area of Flux Pattern. Right—Light Area of Flux Pattern.

steel surface on which it was formed. That this is actually the case becomes apparent when the surface of the iron-tin alloy on commercial tin plate is examined at high magnification, Fig. 3A. On removing the alloy, it will be found that a corresponding differential roughness prevailed on the steel base.

Written Discussion: By G. C. Jenison, research chemist, Weirton Steel Co., Weirton, West Va.

The author has presented some very interesting data concerning a subject that is not fully understood. While the composition of the tin-iron alloy is fairly well defined, there are still many questions that remain unanswered relative to the rate of formation, and conditions under which it is formed. The proposed method should stimulate further study of the subject.

We agree with the author that present chemical methods are not entirely satisfactory for this work, and that microscopic methods are rather difficult to carry out during a study of this kind.

It is unfortunate that the data presented in Figs. 2, 3, 4 and 5 were not

verified, or at least compared with chemical data which might have been obtained from the analysis of the specimens tinned during the work.

It should be pointed out that regular tin plate stock varies in thickness from 0.007 to 0.011 inch, and even greater thicknesses are not uncommon. It would seem that these wide variations in thickness, with attendant variations in thermal conductivity, would influence the rate of alloy formation, particularly in the initial stages.

Further consideration might be given to the chemical analysis of the specimens. There are a number of ranges of analysis in the stock going into tin plate, particularly in phosphorus and copper. It would be interesting to know the thickness of alloy produced in unit time at the temperatures investigated for steels in phosphorus content ranges of 0.008 to 0.012 per cent; 0.040 to 0.060 per cent and 0.080 to 0.100 per cent, in addition to the amount of phosphorus in the samples making up the present paper. Since the copper content of the samples in this paper is not revealed, interest would be in the 0.01 to 0.03 per cent; 0.07 to 0.10 per cent; 0.14 to 0.18 per cent and 0.20 to 0.30 per cent ranges.

Another variable is injected into the problem, with consideration of methods of treatment of the steel prior to tinning. These would include method of reduction, whether cold or hot, annealing and tempering. Variations in any of these operations would result in differences in surface properties of the steel. In this connection, did the author determine which pre-annealing treatment gave the more consistent results mentioned?

We wish to inquire whether the author supplemented his tests with microscopic examination of the alloy formed. In view of the extended time intervals employed, the possibility of changes in the structure of the coating due to diffusion is presented. Microscopic examination of the specimens immersed for longer periods of time would be of theoretical interest.

We feel that the author has made a good opening attack on this problem and we have presented a few practical aspects that should be considered in the event of future studies on this subject. While the technique employed is not directly applicable yet to the problems encountered in the hot-dipping of sheet steel, it is possible that refinements will be found where the rates of formation of tin-iron alloy can be determined in the desired time interval range of seconds rather than minutes.

Author's Reply

The method described in the paper is, of course, not suitable for following the course of the formation of the tin-iron alloy in the brief interval during which steel is in contact with tin in commercial tinning. I agree with Dr. Van Fleet that, if such a method were possible, it would be of great interest. Aside from the difficulties in measuring any quantity in a continuous manner in so short an interval of time, great sensitivity would also be required in order to detect the very slight reduction in iron thickness.

In regard to the sulphur content of the steel, it seems very unlikely that

doubling or halving the sulphur content would have an appreciable effect on the rate of tin-iron alloy formation. During the course of a few experiments not described in the paper, the rate of tin-iron alloy was measured on steel containing 1.03 per cent carbon and 0.25 per cent silicon, and also on steel of 0.28 per cent carbon and 0.12 per cent silicon. In both cases, the A value (thickness of $FeSn_2$ formed in one minute) was within 20 per cent of the value obtained with the tin can stock, and the slopes of the log thickness-log time plot were very close to one half.

These circumstances would lead one to suspect that the rate of $FeSn_2$ formation is relatively insensitive to minor variations in the composition of the steel.

As for the purity of the tin, this also is probably unimportant even for fairly large degrees of contamination. It will be noted that lead is the major impurity. An experiment was carried out at 625 degrees Fahr., using an alloy of 70 lead-30 tin, employing exactly the same procedure described in the paper.

The A value in this case was one-fifth that obtained with pure tin. Although this alloy was preponderately lead, the A value was still of about the same order of magnitude as with tin. Hence the presence of 0.15 per cent lead would hardly be expected to make much difference.

The pictures shown by Dr. Rowland of the tin-iron alloy surface and the steel surface are of considerable interest both from a theoretical and practical standpoint. It is to be hoped that further work may be published in which the continuity and form of the alloy layer are correlated with type of plate, corrosion resistance, etc.

The remarks of Dr. Rowland regarding the detachment of the alloy layer with increasing temperature are undoubtedly true. In some unpublished work in which higher temperatures were employed than those described in the paper, the tin-iron alloy appeared to fall off the steel almost as rapidly as it was formed. In such a case, the slope of the log thickness-log time plot approaches 1, instead of ½, indicating that the amount of the alloy layer formed is directly proportional to time, instead of the square root of time. At 625 and 650 degrees Fahr. (330 and 345 degrees Cent.), no excessive or even marked detachment of the alloy layer seemed to occur, presumably because the specimens were held motionless in the tin bath.

There is no question that good photomicrographs of the tin-iron alloy layer can be prepared. Dr. Rowland has very ably demonstrated this. However, in this work it was desired to obtain a figure for the total amount of $FeSn_2$ formed. Because of the tendency for $FeSn_2$ detachment which has already been discussed, metallographic methods which measure only the $FeSn_2$ on the steel are not suitable. Secondly, there can be no question that the magnetic method offers a more rapid method of test than the metallographic method.

Chemical methods, as suggested by Mr. Jenison, were not used as a check in this work because it was considered that chemical methods are not sufficiently accurate to be useful as a check. It was because of the uncertainties and difficulties of the chemical methods that the magnetic method was developed.

In regard to variations in thickness of tin plate stock, such variations

would not make any difference in the results reported if the specimens were brought up to temperature in a space of time which was sufficiently small compared to the first measured time interval. It is probably true that in commercial tinning where the steel passes through the tin pot in a matter of seconds, variations in steel thickness would be expected to have some effect because of failure of the thicker sheets to attain the bath temperature as readily as the thin sheets.

Variations in the phosphorus and copper contents would be expected to have a minor but possibly measurable effect on the rate of formation of the tin-iron alloy layer. It would be interesting to know exactly what effect all of the common impurities in steel have on tin-iron alloy formation.

The steel used in the work was reported to be cold reduced, but unfortunately, no information as to its mechanical and thermal history is available. The annealing treatments described in the paper, and carried out on the specimens prior to pickling and tinning did not appear to be essential, and apparently did not affect the results much. However, all that can be said is that these annealing treatments, which were carried out in air, appeared to allow more reproducible results. The exact temperature and time were apparently not important. It was, perhaps, just a question of stress relief, but this is only speculation.

THE SOLUBILITY OF IRON OXIDE IN LIQUID IRON

By John Chipman and Karl L. Fetters

Abstract

The equilibria between liquid iron and simple iron oxide slags have been studied by methods utilizing induction heating creating rapid stirring at the slag-metal interface but leaving the slag-gas interface relatively quiet.

Within the limits of the investigation, the oxygen content of the metal was found to be independent of the reducing or oxidizing nature of the atmosphere at the slag-gas interface and independent of the purity of the iron oxide slag when the total FeO content of the slag is in excess of 90 per cent. The effect of temperature on the oxygen content of liquid iron in equilibrium with slags consisting principally of iron oxide has been determined.

Ferric oxide is not completely reduced to ferrous oxide by liquid iron. The equilibrium ratio (per cent Fe_2O_3)/(per cent FeO) has been determined at temperatures of interest in steelmaking.

IN the system iron-oxygen, the coexisting liquid phases at high temperature are molten iron containing a small amount of dissolved oxygen and a liquid oxide phase which, upon cooling, may be represented analytically as a mixture of ferrous and ferric oxides. The composition of this oxide phase and its solubility in the molten metal are basic to the study of slag-metal reactions and for this reason the equilibrium between these two phases has been for many years a problem of wide metallurgical interest.

In his classic paper of 1912 in which the principles of thermodynamics were applied to the making of iron and steel, Le Chatelier (1)[1] said: "We accept at 1600 degrees Cent. (2910 degrees Fahr.) a solubility of 1.1 per cent of the oxide corresponding to an oxygen content of 0.244 per cent in the metal." This estimate was apparently based upon the earlier analysis by Ledebur (2) of blown bessemer metal, using the hydrogen-reduction method.

[1]The figures in parentheses pertain to the references appended to this paper.

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. Of the authors, John Chipman is associated with the metallurgical department, Massachusetts Institute of Technology, Cambridge, Mass., and Karl L. Fetters is associated with the metallurgical department, Carnegie Institute of Technology, Pittsburgh. Manuscript received October 10, 1940.

Austin (3) made a series of melts in magnesia crucibles in a small arc furnace with slags consisting principally of iron oxide. The maximum oxygen observed was 0.288 per cent. No temperature is given, although it would be of little consequence since the 2-kilogram melts were cast into clay pots, a practice which would not tend to prevent the loss of some iron oxide during cooling and solidification.

In a very brief report of the Bureau of Standards (4) it was stated that electrolytic iron melted under the oxidizing influence of still air contained 0.21 per cent oxygen.

Tritton and Hanson (5) made a series of melts of electrolytic iron and iron oxide in magnesia crucibles in an atmosphere of nitrogen. Their results showed a solubility of 0.21 per cent oxygen in iron at the melting point.

Herty and co-workers (6) made a series of experiments to establish the influence of temperature on the solubility of oxygen in iron. Fifty-pound melts of iron were made in magnesia crucibles in a high frequency induction furnace. The metal samples were dipped with a steel spoon and poured into a wedge-shaped steel mold to insure rapid cooling. No attempt was made to maintain an atmosphere other than air over the bath. All temperature determinations were made with an optical pyrometer. In the presentation of their results they calculated the total percentage of FeO in their slags as FeO + 1.35 Fe_2O_3 and corrected the observed percentage of oxygen in the metal to that theoretically present at 100 per cent iron oxide in the slag.

Körber and co-workers (7) reported the solubility of oxygen in iron under iron oxide slags. Their melts were made in small magnesia crucibles (up to 350 grams) in a high frequency induction furnace. Temperature measurements were made with an optical pyrometer sighted on the bare metal, and occasionally checked with a platinum thermocouple in a silica protection tube. Both slag and metal were in contact with air. Some of their tests were dipped in small molds to insure quick cooling, whereas other tests were cast. There did not appear to be any difference in the results obtained with the two sampling methods at moderate temperatures. The results were expressed as the ratio

$$\frac{[O] \times 100}{(FeO)}$$

where the FeO of the slag was obtained by calculating the total iron of the slag to FeO. The results of their work agreed quite well with those of Herty and co-workers.

It has appeared desirable to combine some of the experimental features of these previous workers with certain refinements in tech-

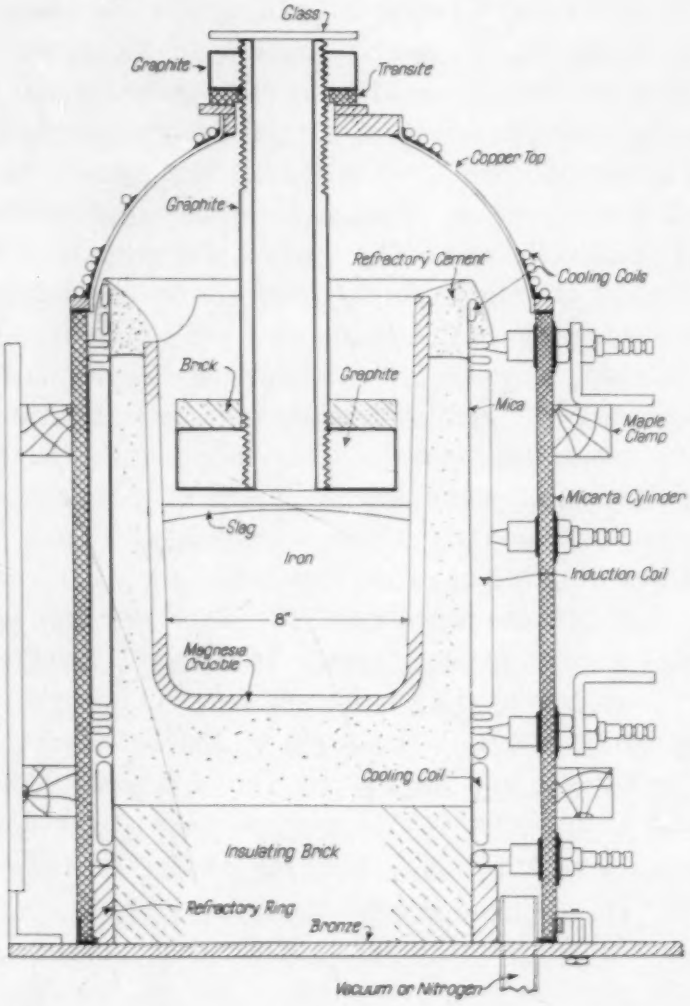

Fig. 1—Induction Furnace Built for the Study of Slag-Metal Equilibria.

nique to redetermine the solubility of oxygen in iron under slags consisting essentially of iron oxide. Among the desired precautions have been the full obtainment of equilibrium by prolonged contact, the exclusion of the effects of atmospheric oxidation, the rapid solidification of samples, and temperature measurements by thermoelectric means.

Experimental Methods

A high frequency induction furnace arranged for melting in vacuum or controlled atmosphere was especially designed and constructed for studies of slag-metal equilibria. This furnace, which is shown in Fig. 1, has a capacity of 150 pounds but is ordinarily charged with only 65 to 70 pounds to bring the slag line to the level indicated in the figure. To prevent cooling of the upper surface of the slag a graphite disk, covered by insulating brick, was suspended from a graphite tube a few centimeters above the slag level. The disk, being made of conducting material, was heated by induction and attained a temperature about 100 to 200 degrees Cent. lower than that of the metal itself. The heating characteristics of the disk were improved by cutting a deep annular groove and filling this with a ring of molybdenum formed by many layers of thin strip. During the vacuum melting stage of each experiment this slag heater and its supporting sleeve were removed and the top of the furnace dome was closed by a pyrex glass disk. In certain experiments, as will be noted later, this heater was omitted; in others it was replaced by a grid of silicon carbide rods which were heated electrically to approximately the temperature of the metal.

In carrying out an experiment 30 kilograms (66 pounds) of ingot iron was charged in the furnace. In each run using a new crucible this was supplemented by a charge of 1 to 2 kilograms of ferric oxide to completely saturate the walls of the crucible. The charge was melted in vacuum and the pumping continued until the pressure was reduced to 3 millimeters or lower. Air was then admitted, the cover removed and any metal adhering to the crucible wall was melted down with oxygen. Additions of ferric oxide were made if necessary to cover the metal surface and the cover was then replaced, along with the graphite sleeve and disk. Nitrogen was then admitted to the furnace and its flow was continued at the rate of about 5 liters per minute during the course of the run. For this purpose tank nitrogen was passed through a tube containing copper at about 400 degrees Cent. (750 degrees Fahr.) to remove oxygen. The flow of gas was upward around the coil, downward in the furnace around the disk, and upward through the graphite tube. Some air inevitably entered the furnace during sampling and temperature measurement, but the general effectiveness of the system in preventing oxidation

of the slag is evidenced by the fact that only a slight oxidation of the graphite disk occurred.

Temperature measurements were made and samples were secured at intervals of 30 to 60 minutes during the course of the run which generally lasted 6 to 10 hours. The minimum time allowed for establishment of equilibrium after an addition or a change in temperature was 30 minutes.

Temperature Measurements—Temperatures were measured by means of tungsten-molybdenum thermocouples inserted into the metal in magnesia or silica protection tubes. These couples which were described by Osann and Schröder (8) and used by Leiber (9) in open-hearth studies have given good service in this laboratory during the past two years. The commercial wires have been found to be uniform within a given lot, though different lots differ in characteristics and the thermal e.m.f. curve of each lot must be determined by experiment. Wires 0.020 to 0.025 inch in diameter (0.50 to 0.65 millimeter) have been found satisfactory. Couples are made by twisting the molybdenum wire around the tungsten and arcing the tip to a carbon electrode. The couples are then annealed and straightened by heating them electrically to about 2500 degrees Cent. (4530 degrees Fahr.) in an atmosphere of hydrogen. They were calibrated at the melting points of copper, nickel, iron and palladium and further checked up to 1750 degrees Cent. (3180 degrees Fahr.) by comparison with platinum-platinum, rhodium couples.

The protection tubes used in the present investigation were usually made of sintered magnesia using a method similar to that described by Barrett and Holbrook (10). The tubes as sintered are rather porous and it is difficult to obtain a satisfactory e.m.f. indication before the penetration of iron oxide has destroyed the couple. The sintered tubes may, however, be coated with an alcoholic magnesia slip similar to that used by Thompson and Mallett (11) for the casting of crucibles. The coated tubes after air drying at 100 degrees Cent. will generally resist penetration by iron oxide slags for one or more temperature determinations. In a few instances where the later slags to be studied in a particular melt did not preclude small additions of silica, the desired slag and metal tests were taken and then the temperature was determined, using fused silica protection tubes. These tubes permitted a satisfactory measurement before they were dissolved by the iron oxide slags.

Sampling—The slag and metal samples were obtained by dipping a small, long handled mold through the sleeve that supported the slag heater. The samples, either slag or metal, were allowed to solidify in the upper part of the furnace in the atmosphere of nitrogen. The molds were made of 2-inch lengths of pipe, split longitudinally to facilitate removal of the sample and held together by iron wire. In the early experiments 1-inch standard pipe was used for both slag and metal samplers. It was found, however, that some segregation had occurred in metal samples obtained at temperatures above 1650 degrees Cent. (3000 degrees Fahr.). To provide more rapid cooling of these samples, molds were made from pipes of smaller diameter and heavier wall. The diameters and wall thicknesses in millimeters were approximately: (a) 23 by 4 wall; (b) 16 by 4 wall; (c) 13 by 5.5 wall. Comparison of the oxygen content of simultaneous samples in the three molds showed that below about 1650 degrees Cent. (3000 degrees Fahr.) the three samples gave the same results. At high temperatures the results of (b) and (c) were the same, but the larger mold gave lower results.

In all cases reported here the samples were entirely sound and only slightly piped at the extreme top. This may be credited to the vacuum melting of the heat which removed hydrogen and nitrogen and reduced the carbon content to about 0.004 per cent. Numerous carbon analyses were made on samples taken during many heats and

Table I
Check Tests on Samples

Heat No.	Test No.	Temperature Degrees Cent.	Per Cent Oxygen	
			B. of S. (1 Gram Samples)	M.I.T. (5 Gram Samples)
E24	2	1525	0.19/0.19	0.182/0.200/0.175
E21	2	1592	0.22/0.22	0.230/0.215
E25	4	1715	0.26/0.26/0.32	0.304/0.298
E28	1	1620	0.212/0.236	0.231/0.236
E28	9	1615	0.207/0.230	0.252/0.222/0.216
E28	13	1623	0.238/0.207	0.225/0.222

the results never exceeded 0.007 per cent. Similarly, the nitrogen content remained 0.002 to 0.004 per cent, indicating complete protection of the metal by the slag layer.

Analyses—All oxygen analyses were made by the vacuum fusion method in the apparatus described by Chipman and Marshall (12). In most instances duplicate samples agreed within 0.01 per cent oxygen, and in cases of greater discrepancy additional checks were made. The accuracy of the method was checked by occasional

analyses of sample No. 7 from the co-operative study of methods for determination of oxygen in iron (13). As a further check six samples were sent to the Bureau of Standards where they were analyzed by a similar method through the kindness of Dr. J. G. Thompson. The results of the comparison are given in Table I.

Regarding the slag analyses it may be mentioned that iron oxides were determined by titration of total iron and ferrous iron, the ferric oxide being determined by difference. A correction was applied to take into account the reduction of ferric oxide by sulphur during the analysis as suggested by Maurer and Haderer (14). It should be noted that, although the total iron content is determined with precision, the ferric oxide is subject to larger analytical errors than are other components of the slag.

Typical Experiment—The making of a typical experimental melt will be described to indicate the procedure followed. Heat E-17 was made in a new magnesia crucible. Thirty-two kilograms (70 pounds) of iron was charged, partly ingots from previous heats and partly ingot iron as-received. One and a half kilograms of ferric oxide was also charged. This particular heat was melted under air, then the vacuum applied. After pumping for a sufficient time to attain a pressure of about 3 millimeters, nitrogen was admitted, the top was taken off, slag and metal samples were secured immediately and the metal temperature was measured. In this heat a simple insulating brick cover was used instead of the graphite disk. Above this was placed the furnace cover, the nitrogen flow was started and an hour and a half allowed for the attainment of equilibrium conditions. The temperature was then measured and slag and metal samples were taken. The power input was increased for a 10-minute period, then held steady for 1 hour, after which the next samples and temperature measurement were taken. After metal sample No. 7 the slag covering on the metal was insufficient to completely cover the molten iron; an addition of 500 grams of ferric oxide was made and 35 minutes was allowed before taking the next samples. The heat was continued until eight pairs of samples had been taken with accompanying temperature measurements, conditions in every case being held steady during at least 30 minutes before sampling. The total time of this heat was 10 hours. The remaining metal was cast without deoxidation into small ingots which solidified without gas evolution.

Table II
Summary of Experimental Data

Sample No.		Temperature Degrees Cent.	Oxygen in Metal Per Cent	Slag Analysis CaO	SiO_2	FeO	Fe_2O_3	FeO_t	MgO	Notes	
E–13–	2	1577	0.192	1.54	1.20	87.78	6.73	93.83	3.23	a	
	4	1560	0.189	1.71	1.34	87.22	6.88	93.41	3.06	a	S
	6	1621	0.241	2.02	1.52	86.23	5.94	91.58	4.07	a	
	8	1670	0.267	2.50	1.72	82.99	6.26	88.63	6.30	a	
	10	1680	0.277	1.46	1.10	87.36	5.47	92.28	4.26	a	
E–17–	2	1617	0.219	0.37	1.46	87.54	5.92	92.86	4.11	a	V
	4	1619	0.241	0.23	1.42	87.50	5.22	94.20	3.06	a	
	5	1731	0.245	0.25	1.48	88.71	4.27	92.55	5.10	a	S
	7	1757	0.346	0.33	1.60	88.17	3.66	91.47	5.74	a	S
	9	1754	0.290	0.31	1.54	88.40	3.74	91.77	5.87	a	S
	12	1701	0.308	0.21	1.68	88.48	4.35	92.80	5.04	a	
	17	1661	0.262	0.35	1.96	87.85	4.70	92.08	4.72	a	
E–18–	2	1654	0.245	tr.	0.64	90.49	5.74	95.65	3.03	a	
	4	1590	0.216	tr.	0.72	90.39	5.86	95.67	2.69	a	
E–19–	2	1623	0.240	tr.	0.92	88.45	6.92	94.68	3.85	a	
E–20–	2	1593	0.229	0.82	1.18	85.72	6.07	91.17	6.20	a	
E–21–	2	1592	0.223	tr.	1.54	86.83	6.73	92.88	3.79	a	
	4	1600	0.231	tr.	1.74	86.42	6.57	92.33	3.89	a	
E–22–	2	1545	0.183	0.60	0.48	90.50	6.26	96.14	2.44	a	
	4	1643	0.264	0.99	0.76	89.32	5.76	94.51	3.86	b	
E–24–2,	4	1525	0.184	tr.	0.60	91.73	5.14	96.43	2.29	a, b	
	6	1810	0.384	tr.	0.98	89.22	2.49	91.28	7.15	c	
E–25–2,	4	1715	0.300	tr.	0.54	88.61	4.74	92.87	6.08	b, c	
E–28–	1	1620	0.232	tr.	0.58	89.20	6.27	94.85	3.85	c	V
	3	(1575)	0.203	tr.	0.36	90.96	6.11	96.47	2.72	b	O
	5	1572	0.186	tr.	0.50	91.21	5.60	96.27	2.62	b	A
	7	1578	0.181	tr.	....	.....	....	.....	....	b	
	9	1615	0.220	tr.	0.48	90.81	5.83	96.08	2.92	c	
	11	1630	0.238	tr.	0.50	90.40	5.94	95.74	3.53	b	H
	13	1623	0.223	tr.	0.54	90.71	5.21	95.42	3.44	b	H
	15	1600	0.211	tr.	0.68	90.35	6.22	95.96	3.21	b	A
	16	(1580)	0.217	tr.	....	.....	....	.....	....	c	S, O
	18	1600	0.215	tr.	0.56	90.50	5.72	95.66	3.17	b	A

a, b, c. Sampling spoons respectively 23, 16, 13 m.m. inside diameter.
S. Segregated samples. Oxygen value recorded is average of lowest oxygen analyses. Result not considered dependable.
V. Sample dipped immediately after breaking vacuum.
O. Samples within 4 minutes after addition of Fe_2O_3.
A. Bath exposed to air for 30 to 60 minutes before sampling.
H. Bath exposed to H_2-N_2 mixture for 30 to 60 minutes before sampling.

Experimental Results

The data of ten experimental heats are shown in Table II. Three of these heats were made solely to determine the solubility of iron oxide in iron. The seven other heats were used in studies of lime-silica-iron oxide slags and the samples recorded in Table II were taken before additions of lime and silica.

Solubility of oxygen in iron—It has been customary in the past to express the solubility of iron oxide as the calculated percentage of oxygen or of FeO in the metal when the slag consists entirely of iron oxides. On account of the solubility of refractories this condition cannot be realized in practice but the calculation is made on the as-

sumption of a constant distribution ratio. The results of our experiments over a wide range of slag compositions in the lime-silica-iron oxide system show that the distribution ratio of iron oxide between slag and metal is by no means constant. This ratio changes with slag

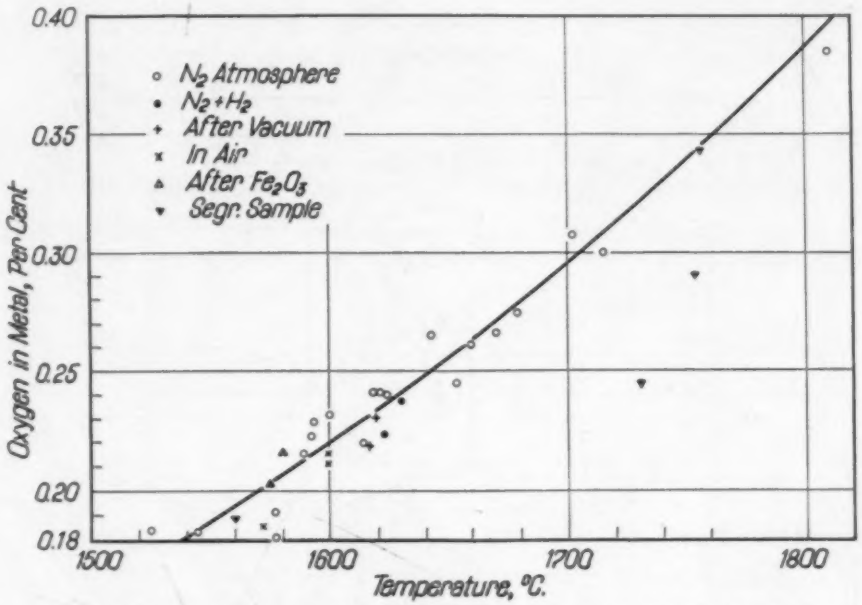

Fig. 2—Effect of Temperature upon Oxygen Content of Liquid Metal.

composition in such a way that as the slag composition approaches pure iron oxide the oxygen content of the metal, rather than the ratio, approaches a constant value. We have found no consistent difference in the oxygen content of liquid iron under slags of 96 per cent total iron oxides as compared with slags containing only 90 per cent. The calculation of a distribution "constant" would therefore be unjustified and the results will be reported simply as the percentage of oxygen in the metal. This is plotted against temperature in Fig. 2. The limiting solubility under a pure iron oxide slag will be greater by an amount which is less than the experimental errors of this investigation.

Theoretically a straight line relationship is expected when the logarithm of the solubility is plotted against the reciprocal of the absolute temperature. Such a plot is shown in Fig. 3. The equation of the straight line is

$$\log \text{ per cent oxygen} = -4860/T + 1.935.$$

Comparison with previous work—The results of Herty and Körber are also shown, each being expressed as a distribution ratio

as originally reported. We have endeavored to account for the wide discrepancy between the old and the new data but have been unable to do so to our own satisfaction. The principal sources of error and a comparison of the methods of dealing with each will be briefly considered. Previous workers measured temperatures optically. Our

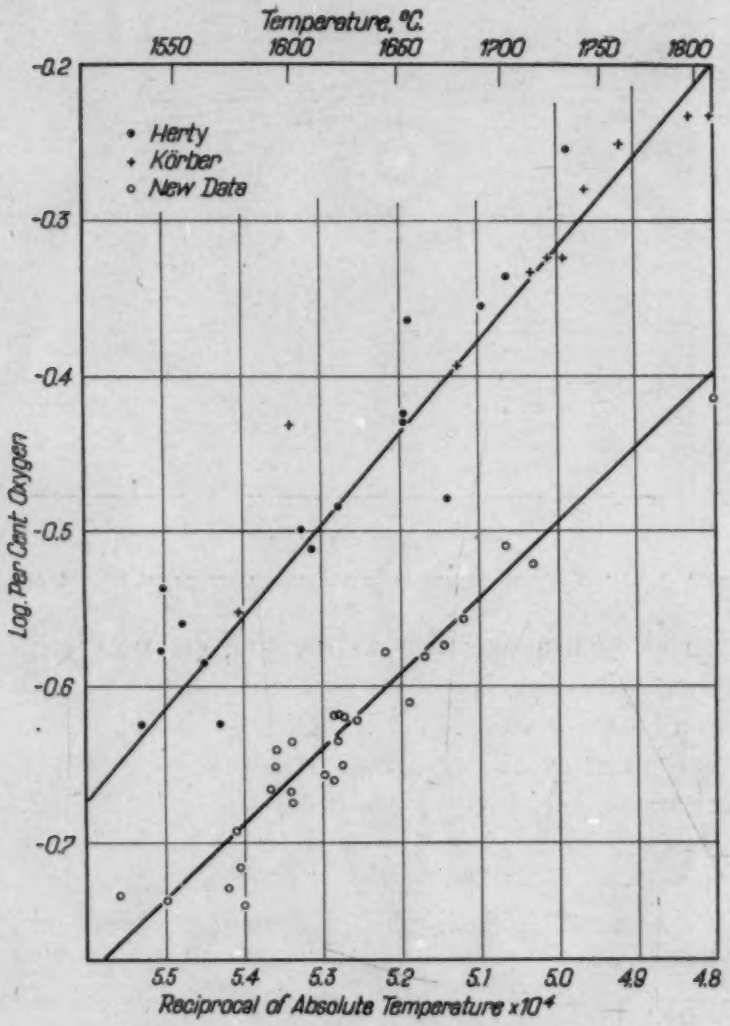

Fig. 3—Solubility of Iron Oxide in Liquid Iron.
Upper line, data of Herty (solid circles) and Körber (crosses). Lower line, average of our results (omitting segregated samples).

measurements with tungsten-molybdenum couples were checked occasionally with platinum-platinum, rhodium couples, the agreement being within ± 10 degrees Cent.; it seems unlikely that our errors in temperature measurement could have exceeded 20 degrees except at the highest temperatures. Previous workers obtained samples by

dipping and pouring into a mold or by permitting solidification in the crucible. Our method of dipping the mold into the bath gives rapid solidification without exposure to air. This is important because slow solidification permits the escape of proeutectic oxide, and repouring may introduce oxides from atmospheric oxidation or entrained slag. Our samples were not always free from entrained slag as shown by occasional high oxygen results. Pieces for analysis were

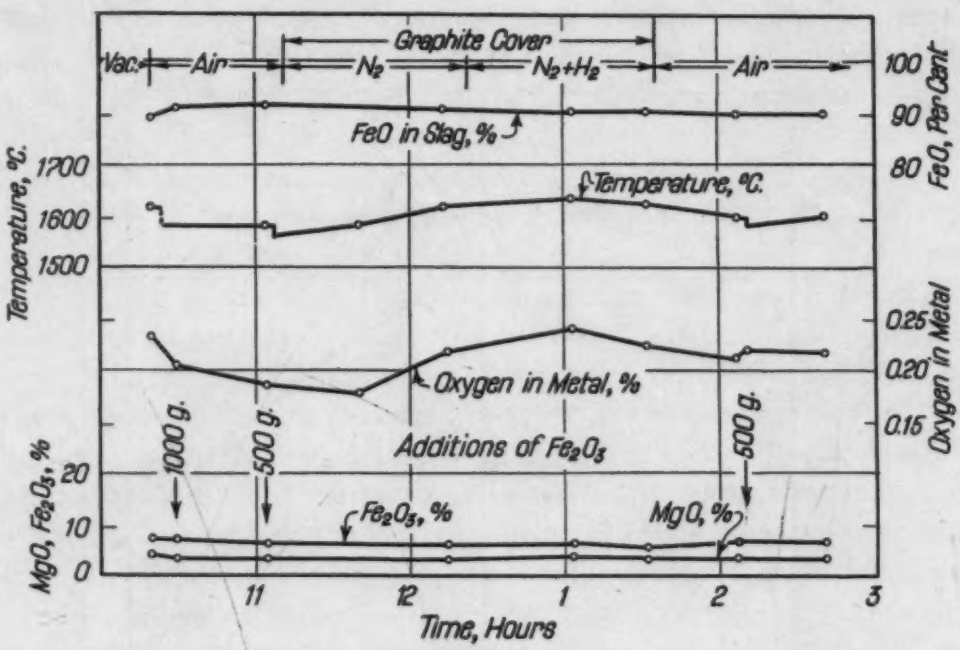

Fig. 4—Graphical Log of Heat E-28.

carefully inspected for visible slag particles which were ground out before analysis. It generally happened that, when two widely divergent results were obtained, repetition of the analysis confirmed the lower result. The duplication of analyses constitutes the best safeguard against the error of entrapped slag.

The time allowed for attainment of equilibrium was longer than in previously published work. Evidence that equilibrium was substantially attained is found in the agreement of samples taken after raising and after lowering the temperature. Slow absorption of iron oxide by the crucible walls or its subsequent release to the metal could have had only a minor influence but may have been responsible in part for the scatter of the results. This conclusion is supported by the observation that Heats 17, 21, 24 and 28, which were made

in new crucibles, gave results which were not consistently lower or higher than those obtained in crucibles that had been used for two or three heats.

Effect of Furnace Atmosphere—The outstanding difference between our technique and that of the other observers is in the control of the atmosphere above the melt. Herty and Körber exposed their melts to air and Herty's slags contained as much as 17 per cent ferric oxide compared to less than 7 per cent in ours. It was chiefly to investigate this effect that our Heat E-28 was made. In this heat

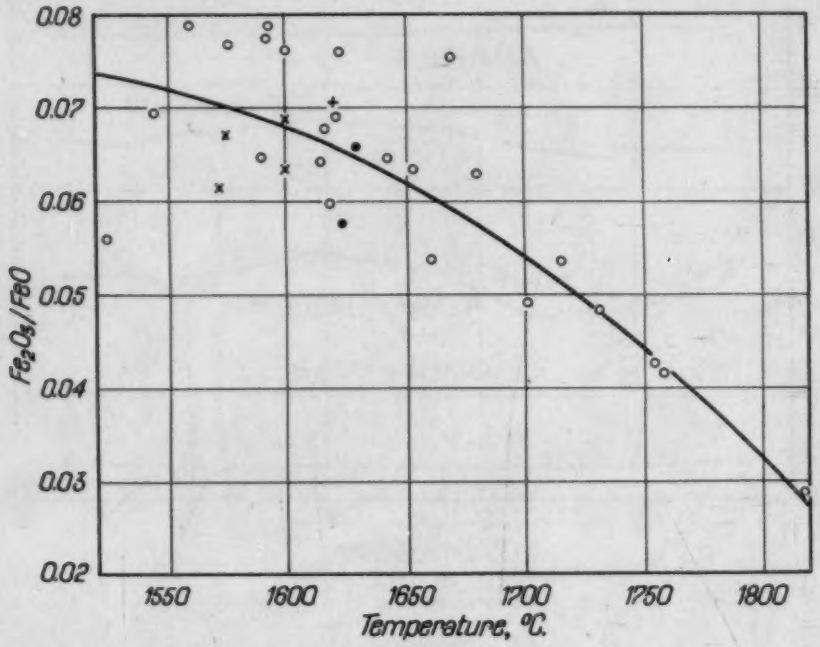

Fig. 5—Ratio of Ferric to Ferrous Oxide (by weight) in the Slag. Symbols the same as in Fig. 2.

several conditions of oxidation and reduction were investigated. The first sample was taken within 45 seconds after admitting air to the vacuum furnace. Other samples were taken after ferric oxide additions and after prolonged exposure to air, the crucible being covered with a refractory brick having a 2-inch hole. After prolonged flushing with nitrogen, several samples were secured under an atmosphere consisting of 7 per cent hydrogen, balance nitrogen containing 0.3 per cent oxygen, which should be strongly reducing to the oxygen-saturated iron. The complete record of this heat is shown graphically in Fig. 4 and the results obtained under the different atmospheric conditions are shown by the various symbols in Fig. 2.

Contrary to expectations, the results obtained in air were not significantly different from those found under a nitrogen atmosphere or under a mixture of nitrogen and hydrogen. Both in regard to the oxygen content of the metal and the ferric oxide content of the slag (Fig. 5) these points fell within the normal scatter of results obtained in nitrogen. It seems probable also that there were actual atmospheric variations in many of the earlier heats which were not reflected in the results. The graphite disk should convert any oxygen in the nitrogen to carbon monoxide, thus creating a reducing atmosphere. In runs 18, 19 and 22, silicon carbide rods, which are practically inert, were substituted for graphite and in 17 no heater at all was used. Yet, these results are not characteristically higher or lower than the others.

These results must not be interpreted as showing that the slag composition is always independent of the atmosphere. The surface layer of slag is undoubtedly affected by the atmosphere but under the conditions of our experiments this layer is stagnant and it is in contact with a quiet gas. Reactions under these conditions are slow. The slag-metal interface on the contrary is subject to rapid motion, due to the stirring effect of induction heating, and here the reaction rate is high. Equilibrium is closely approached at the slag-metal interface, but the bulk of the slag is far from being in equilibrium with the gas. It is for these reasons that, under our experimental conditions, the oxygen content of the metal is independent of the atmosphere above the slag. We obtained no data on the effect of direct exposure of the metal to oxidizing atmospheres but it seems possible that such direct exposure is accountable for the higher oxygen content observed by Herty and by Körber.

Ferric oxide in the slag—It has often been assumed that at the slag-metal interface all ferric oxide in the slag is reduced to ferrous oxide. Although this reduction of Fe_2O_3 is an important factor in steelmaking, the data of Table II indicate that the reaction does not go to completion. All of our slags, regardless of the oxidizing or reducing character of the atmosphere, contained between 2.5 and 6.9 per cent ferric oxide and the conclusion seems justified that under equilibrium conditions the slag layer adjacent to the metal would contain approximately this amount. The ratio of ferric to ferrous oxide is affected by temperature as shown in Fig. 5, decreasing at higher temperatures at such a rate as to indicate a composition cor-

responding to FeO at about 1900 degrees Cent. (3450 degrees Fahr.). It will be shown in a subsequent paper that the ratio $(Fe_2O_3)/(FeO)$ is increased by additions of lime and decreased by silica. Within the range of composition included in Table II, however, there is no consistent variation of this ratio with other components of the slag.

Summary

A method for the study of slag-metal equilibria has been developed and applied to liquid iron and simple iron oxide slags. The method utilizes inductive heating which creates rapid stirring at the slag-metal interface while the slag-gas interface is relatively quiet.

The oxygen content of the metal and the ferric oxide content of the bulk of the slag were found to be independent of the oxidizing or reducing character of the gas within the limits investigated.

The oxygen content of the liquid metal is not greatly affected by the purity of the iron oxide slag in the range 91 to 96.5 per cent total FeO. The oxygen content of liquid iron in equilibrium with these slags is given by the equation:

$$\log \text{ per cent oxygen} = -4860/T + 1.935.$$

This equation may be used, within the limits of error of these experiments, to represent the solubility of oxygen under pure iron oxide slags. This result is substantially lower than the formerly accepted solubility.

Ferric oxide is not completely reduced to ferrous oxide by contact with liquid iron. An equilibrium condition is reached in which the ratio $(\%Fe_2O_3)/(\%FeO)$ is about 0.07 at the melting point and decreases with rising temperature to about 0.03 at 1800 degrees Cent. (3270 degrees Fahr.).

Acknowledgments

The authors wish to express their thanks to Messrs. T. B. Winkler and Shadburn Marshall for assistance in making the experimental heats and calibration of the thermocouples, and to D. L. Guernsey for the analyses of the slags and many of the metal samples. Also, to Dr. J. G. Thompson of the Bureau of Standards for his checks of our vacuum-fusion oxygen determinations. Without this confirmation we would have hesitated to publish results so radically different from the formerly accepted solubility.

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DISCUSSION

Written Discussion: By Frank G. Norris, metallurgist, Wheeling Steel Corp., Steubenville, Ohio.

It has been a long time since Bulletin 34 was written on this same subject and many improvements in experimental and analytical methods have been made. Some of these improvements have resulted in a more accurate definition of experimental conditions. It seems that the lower values of this investigation represent the true solubility of FeO in iron under pure iron oxide slags. It is hoped that this new determination will be the foundation of as much progress in the understanding of slag-metal relations as was the older one. In view of the fact that the effect of lime additions has not yet been reported, what are

the authors' suggestions for applying the new solubility data to working conditions? In other words, how should practical concepts be revised to conform to the lower values?

In view of the space limitations of the technical press and the increasing tendency to restrict pertinent data to micro film, the Publication Committee of the American Society for Metals is to be thanked for allowing the publication of the data both as figures and tables as well as the discussion. Publication of papers such as this increases the value of A.S.M. membership and it is hoped that this policy will be continued.

Oral Discussion

L. S. DARKEN:[1] These new values for the solubility of iron oxide in molten iron presented in this paper and in a previous one by the same authors undoubtedly represent the results of the most careful investigation to date on this subject. As shown by Marshall and Chipman, the use of these data cuts down the discrepancy between the equilibrium oxygen pressure of the system iron-iron oxide at the melting point of iron as determined from temperatures above and below the melting point. This fact increases confidence in the values reported in this paper. Nevertheless the discrepancy (amounting to about 50 per cent) between the present values and older values of Herty and Körber for the solubility is somewhat disconcerting, especially since the authors admit that they cannot satisfactorily account for it.

An investigation of the temperature-pressure-composition relationships of the oxides of iron has been conducted at our laboratory. As a part of this investigation iron oxide was melted and held at various temperatures in closed iron crucibles. Analyses of the quenched product were taken to represent the composition of the molten oxide equilibrium with iron. Near the melting point of iron the ratio of ferric to ferrous oxide was found to be about 0.055. This is in reasonably good agreement with the value reported in the present paper (about 0.072). The minor discrepancy is undoubtedly occasioned by the magnesia present in the melts of Chipman and Fetters. Magnesia tends to form ferrites—in much the same way as lime—and thus probably increases appreciably the amount of ferric oxide above that which would be present in the absence of magnesia.

Authors' Reply

We think Dr. Darken's explanation of the discrepancy in Fe_2O_3 is perfectly sound and correct. Magnesia undoubtedly stabilizes Fe_2O_3.

Mr. Norris raises the question of the effects of other ingredients. Attention is called to the fact that this is only the first paper of a series. The second paper will contain extensive data on slags containing lime, silica and iron oxides. This second paper was published last February and in it will be found the answer to Mr. Norris' question.

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[1]United States Steel Corp., Research Laboratories, Kearny, N. J.

MAGNETIC METHODS FOR DETERMINING CARBON IN STEEL[1]

By B. A. Rogers, Karl Wentzel, and J. P. Riott

Abstract

Consideration was given to five magnetic properties of steel that seemed likely to vary with carbon content in a definite manner—saturation, permeability, coercive force, remanence, and hysteresis loss. The first two were investigated, and the results obtained are reported in some detail. The usefulness of the third had been described previously, but additional studies were made. The last two were not investigated as they did not appear to have any advantage over the other properties.

The experiments showed that magnetic saturation and carbon content could be accurately correlated between the limits of about 0.50 per cent carbon and some undetermined point above 1.10 per cent, but that below 0.50 per cent the saturation-carbon content curve had a slope too small to be satisfactory. A new apparatus employing alternating current was used to measure permeability; by means of a rectifier the values were indicated as a steady deflection on a direct-current meter. With this equipment two types of heat treatment were required; samples containing more than 0.40 per cent carbon were quenched from above the critical range, whereas those with less were kept in the mold until they were below the critical range. When both types of heat treatment were used, samples ranging from below 0.10 per cent to some value above 1.10 per cent carbon could be tested in the apparatus. A brief description is given of a simplified apparatus for determining carbon content from measurements of coercive force.

Introduction

RAPID analysis of the composition of samples taken from the open-hearth is of interest to manufacturers of steel. Carbon

[1]Published by permission of the Director, Bureau of Mines. (Not subject to copyright.)

A paper presented before the Twenty-third Annual Convention of the Society held in Philadelphia, October 20 to 24, 1941. Of the authors, B. A. Rogers is supervising engineer, Metallurgy of Steel Section, Metallurgical Division, Central Experiment Station, Bureau of Mines, Pittsburgh, Karl Wentzel was formerly junior metallurgist, and J. P. Riott is junior chemist of the same section. Manuscript received May 14, 1941.

is of particular importance, and by use of improved equipment the time required for its analysis by chemical means has been greatly reduced. Nonchemical methods of determining carbon—particularly measurements of electrical resistance and magnetic properties—have also been employed successfully. These physical methods give results which can be used to measure the carbon content with sufficient exactness to justify their substitution for final chemical analysis in many cases and to serve as a means of control in almost all melting work.

Possible Magnetic Methods

Before reporting on the work that the authors have done on magnetic apparatus for determining carbon, a brief discussion of the various magnetic properties that can be considered as bases for such methods appears appropriate. Five commonly measured properties which are known to vary with the percentage of carbon, to some degree at least, will be described; these are saturation, permeability, coercive force, remanence, and hysteresis loss. (See Fig. 1.)

Fig. 1a illustrates the familiar fact that the intensity of magnetization in a piece of steel cannot be increased beyond a certain value regardless of the magnetizing force. In the figure this upper limit is indicated by the horizontal dotted line. It should be noted that the ordinates of this graph represent only the flux density B — H ($B - H = 4 \pi I$ where I is the intensity of magnetization) which is attributable to the steel itself and not the total flux density B due to the steel plus the magnetizing field.

Measurements of the magnetic saturation of annealed steels by Esser and Momm (1)[2] indicate that the change of this property with carbon content is too slight to make the method practical for determining carbon. On the other hand, Gumlich's (2) data on quenched fabricated steels show a steady decrease of saturation value with carbon content up to 1 per cent or more and a slower rate of change at higher percentages. However, Gumlich (2), McCance (3), and Esser and Ostermann (4) found for fabricated specimens that, beginning at about 0.90 per cent, the variation of saturation magnetization with temperature of quenching becomes very noticeable in the high range of carbon. This condition, which presumably results from differences in the quantity of retained austenite, sug-

[2]The figures appearing in parentheses refer to the bibliography appended to this paper.

gests special care in handling samples above the eutectoid composition.

The graph of permeability against field strength shown in Fig. 1b has been taken from a paper by Gans (5). In this figure, which represents a hardened, high carbon steel of unspecified composition, the comparatively flat, straight part at the left and the high field strength necessary to reach maximum permeability are prominent

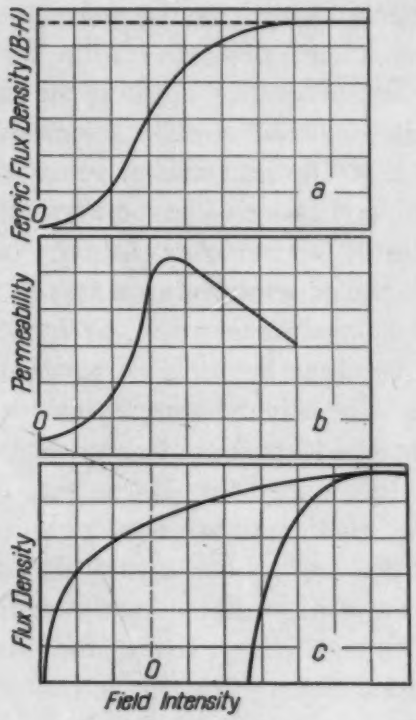

Fig. 1—The Change of Magnetic Properties with Strength of Magnetizing Field.

features. For very small magnetic fields the permeability of a hardened steel increases only slightly with magnetizing force. Thus, when Gumlich and Rogowski (6) increased the field strength 40 times to a final value of 0.4 oersted, the permeability rose only 3 per cent. Experiments on quenched steels by Gumlich (2) showed a consistent decrease in permeability at low field strengths (initial permeability) with rise in carbon content to a point well above 1 per cent. Hence, the evidence favors the measurement of permeability at low field strengths as a rapid means of determining the carbon content. The practicability of using the variation of permeability at some definite magnetizing field to ascertain the percentage of carbon

is obvious from the current use of instruments based on this principle (7-10).[3]

The half of a hysteresis loop shown in Fig. 1c serves as a basis for discussing the three remaining properties. Remanence corresponds to the intercept of the loop on the B (flux-density) axis. It is somewhat smaller, however, than the actual intercept—the residual magnetism as measured in a complete magnetic circuit—because of the demagnetizing effect caused by the poles that exist at the ends of a bar sample. Remanence depends on the shape of the sample as well as its nature. Gumlich's (2) data on the change of remanence with carbon content in quenched steels are somewhat confusing. One type of steel showed a steady decrease of remanence, at a fixed magnetizing field, as the percentage of carbon was increased, but others behaved erratically below 0.5 per cent carbon. Measurements of the remanence of slowly cooled samples as a means of determining carbon content evidently have some merit, as in 1876 a method (11) based on this principle showed sufficient promise to be used for at least several months. The scheme recently employed by Blosjo (12) for samples not quenched through the critical point involves the measurement of the difference between the flux density produced by a definite magnetizing field and that remaining after the removal of the field, that is, the difference between the flux density in the magnetized sample and the remanence. As the remanence is comparatively small for low magnetizing fields, the method approaches a measurement of permeability.

Coercive force is represented in Fig. 1c by the intercept on the H (field-intensity) axis. Work by Curie (13) and Gumlich (2) on quenched, fabricated steels indicated a rise in coercive force with increasing percentages of carbon to a point above 1 per cent. Matsushita's (14) data reveal marked variation in coercive force with temperature of quenching for steels containing more than about 0.80 per cent carbon. Between 0.80 per cent and a carbon content such that the critical range is still below 1472 degrees Fahr. (800 degrees Cent.), this variation is much less important, particularly if the quenching temperature is between 1472 and 1832 degrees Fahr. (800 and 1000 degrees Cent.). Work reported by the authors (15) shows that samples containing less than 0.70 per cent do not

[3]The carbometer (7-9) measures a special kind of permeability. Instead of the magnetizing field being alternated between two numerically equal but oppositely directed values, it is varied between two unequal values of the same sign.

give erratic results due to variation of quenching temperatures when quenched from well above the critical range.

Despite copious data on soft steels, information on the correlation between the area of the hysteresis loop and the carbon content over the ordinary range is insufficient to warrant conclusions concerning a method based on such measurements.

Properties Studied in Present Investigation

Of the five magnetic properties described, three have been investigated by the authors. These are the magnetic saturation; the permeability at low values of field intensity, that is, the initial permeability, and the coercive force. The studies of these properties as bases for methods of determining carbon content have not been complete in every detail but appear to have been carried far enough for present purposes. The apparatus developed and the results obtained with it will be considered in the above order.

The remaining two properties, remanence (or the more simple residual magnetism) and hysteresis loss, were not investigated because methods based on them seemed to offer no advantage over those studied—either in extent of operating range or speed of manipulation. The measurement of hysteresis loss is so time consuming that any method based on it would be relatively impractical.

Relation Between Saturation and Carbon Content

Apparatus—Preliminary experiments demonstrated that the slope of the saturation flux density-carbon content curve for samples not quenched from above the critical range was too flat to be useful. For hardened samples the slope in the region below about 0.50 per cent carbon was again too small to be serviceable, but above this value the rate of change with percentage of carbon was satisfactory. Because of this limitation, the saturation-testing apparatus was used at first mainly in the detection of cavities and other defects in samples employed in other tests. As the saturation flux density is a rather characteristic property, measurements of samples taken under reasonably constant conditions should give consistent results; hence a considerable discrepancy between the readings on any pair of samples was taken as a cause for suspicion. Determinations of saturation values were not made on the samples until they reached the

laboratory. The degree and rapidity with which saturation value changes with time were not studied in detail, but a few tests indicated little alteration over the period concerned.

The apparatus shown in Fig. 2 is designed to measure the intensity of magnetization—or, more exactly, 4π times this value

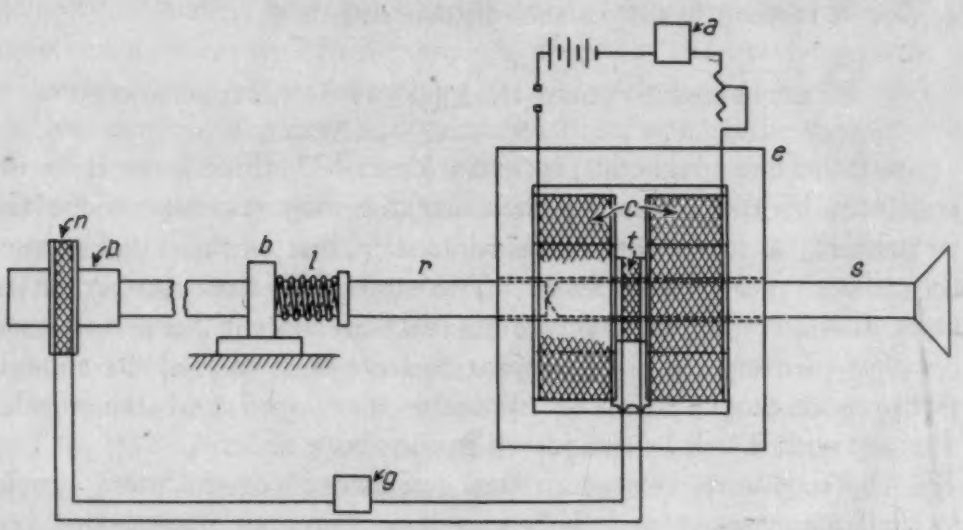

Fig. 2—Apparatus for Determining Carbon from Measurements of Magnetic Saturation.

($4\pi I = B - H$)—of samples subjected to magnetic fields strong enough to produce practical saturation. The measurement is made by placing the sample (located in a strong magnetic field) through a coil which is connected to a ballistic galvanometer, withdrawing it suddenly, and noting the resulting deflection. As the flux due to the magnetizing field is essentially the same whether any steel passes through it or not,[4] the deflection of the galvanometer corresponds to the flux in the sample alone. In the apparatus used, an expansion of the scale was obtained by giving the coil about the sample an excessively large number of turns and then nullifying part of the resulting impulse through the production, simultaneously with the removal of the sample, of an opposing electromotive force. These facts help to clarify the nature and function of the various parts of Fig. 2.

In the figure the electromagnet *e* and sample *s* are drawn to scale, but the remainder of the sketch is schematic. The frame and pole pieces of the magnet are drilled out to receive the sample, which crosses the gap between the pole faces. The magnet is energized by

[4]Actually, the presence of the specimen does influence the magnetizing field to some extent, but the change is small for strong fields and was of no importance in the present experiment.

a current of about 5 amperes—from a storage battery in this instance —through the coils *c*. Regulation of this current by a rheostat need not be exact, as a moderate variation from the usual field intensity—about 2600 oersteds—has little effect on the (B — H) flux density through the sample. Withdrawal of the sample is assisted by the plunger *r* which is urged forward from a position against a stop, not shown, by spring *l*. Not shown also is the second one of the bearings *b* through which *r* slides. The secondary coil *t*, in which is generated the impulse originating in the removal of *s*, is indicated in the gap of the magnet *e*. The impulse in this coil is opposed by another electromotive force developed simultaneously in coil *n* by the movement of Alnico permanent magnet *p* which is attached to plunger *r*.

Procedure—The samples employed in these experiments were of the type frequently used in making magnetic tests for carbon. About 2 pounds of metal were taken from the furnace with a slagged spoon, deoxidized with about 12 inches of 1-millimeter-diameter aluminum wire, and poured into a split mold having a cavity ½ inch in diameter and 5 inches deep. When the metal had solidified the mold was opened and the ingot was seized with a pair of tongs and quenched in water at about 68 degrees Fahr. To improve the accuracy of the measurements, the samples were taken in pairs. A considerable discrepancy in the readings of a pair of samples was taken to mean that at least one sample was defective. Usually this conclusion was confirmed by observing some surface flaw or discovering a concealed cavity, but occasionally the trouble appeared to result from some undetected fault in manipulation.

Before the samples were tested for saturation value, they were used in the alternating-current apparatus described later. This procedure is permissible because the magnetizing force employed in the saturation tests was strong enough to overcome the effects of any previously applied field, thus one set of samples served for experiments in two kinds of apparatus.

Results of Experiments on Saturation—The correlation between saturation value and carbon content is most easily observed by plotting the points on a graph such as Fig. 3. In making this graph, average values of pairs were used; that is, the ordinates are the average saturation values of a pair and the abscissas the corresponding average carbon content as determined by combustion. If one sample of a pair had obvious flaws the remaining sample was repre-

sented by a filled circle instead of the empty circle used to represent an average value for a pair. No points were omitted because of excessive divergence between the readings of members of pairs.

As the graph is simple, little discussion of it is required. As already mentioned, the curve tends to flatten with lower carbon content so that the method is impractical below 0.50 per cent carbon.

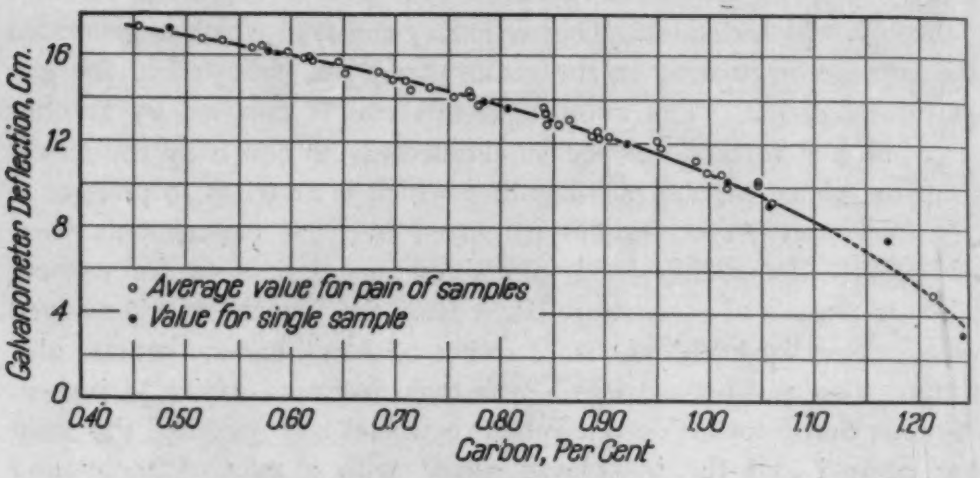

Fig. 3—Deflection-Carbon Content Curve for Saturation Carbon Tester. (Samples quenched immediately).

Above 1.10 per cent carbon, the curve cannot be drawn with assurance because of scarcity of points. From 0.50 to 1.10 per cent carbon, four points deviate from the average curve by distances corresponding to more than 0.02 per cent. No deviation was greater than that corresponding to 0.03 per cent carbon.

Carbon Content from Alternating-Current Measurements

The method of determining carbon content by alternating-current measurements was developed to provide apparatus that would permit reading a pointer in a fixed position rather than by observation of a ballistic instrument. During the development stage, experiments were made with several circuits and various frequencies. The outcome of this work was the circuit shown in Fig. 4 and standardization at 5 cycles per second.[5]

Alternating-Current Apparatus—In the circuit finally selected, the sample is made to function as the center leg of a transformer.

[5]The use of such a low frequency means that the eddy-current effects are reduced to a comparatively small amount.

As shown in Fig. 4, this transformer receives power from a generator and delivers it to an indicating instrument. The sample *s* and the frame of the transformer *t* are drawn approximately to scale, but the electrical circuit, including the primary winding *p* and secondary coils *q*, is indicated schematically. The 5-cycle generator and regulating resistance connected to lines *ll* are not shown. The secondary

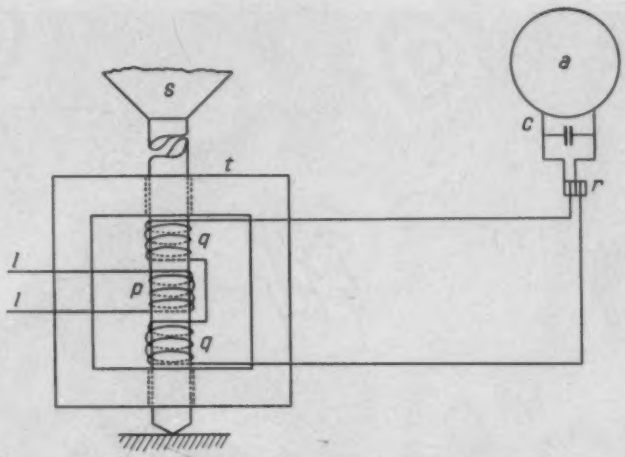

Fig. 4—Apparatus for Determining Carbon by Means of Low Frequency Alternating Current Measurement.

coils deliver power to the 30-microampere direct-current ammeter *a* through a small, copper oxide rectifier *r*. Condenser *c* reduces pulsation of the needle to a point where it is no longer noticeable. The 5-cycle generator has a capacity of 3 watts and is driven by a synchronous motor of 1/75 horsepower. The direct-current field is furnished by Alnico permanent magnets, and although the wave form is not all that could be desired, the generator gives serviceable results.

Fig. 5 is a photograph of the apparatus as finally constructed, excluding the motor-generator set. At the front center is a sample in position for testing and at the extreme left, a standard specimen in an extra cavity. Almost hidden by the sample near the center is a switch for making connections to either of two ranges. This switch was not shown in the circuit of Fig. 4. It is used to cut out some of the turns on the two coils *q* (Fig. 4) when unquenched samples are being tested. The meter and the handle of the rheostat employed for adjusting the primary current are visible at the right. In the front of the cabinet is the dial of the thermometer used to observe the temperature of the apparatus. Because the copper oxide

rectifier is somewhat sensitive to temperature the interior of the cabinet is maintained at a definite temperature by means of heater elements and a thermostat. The small indicator light at the lower right of the panel shows whether the heating current is on.

Procedure—In general, the procedure employed in taking samples was the same as that already described. However, experiments

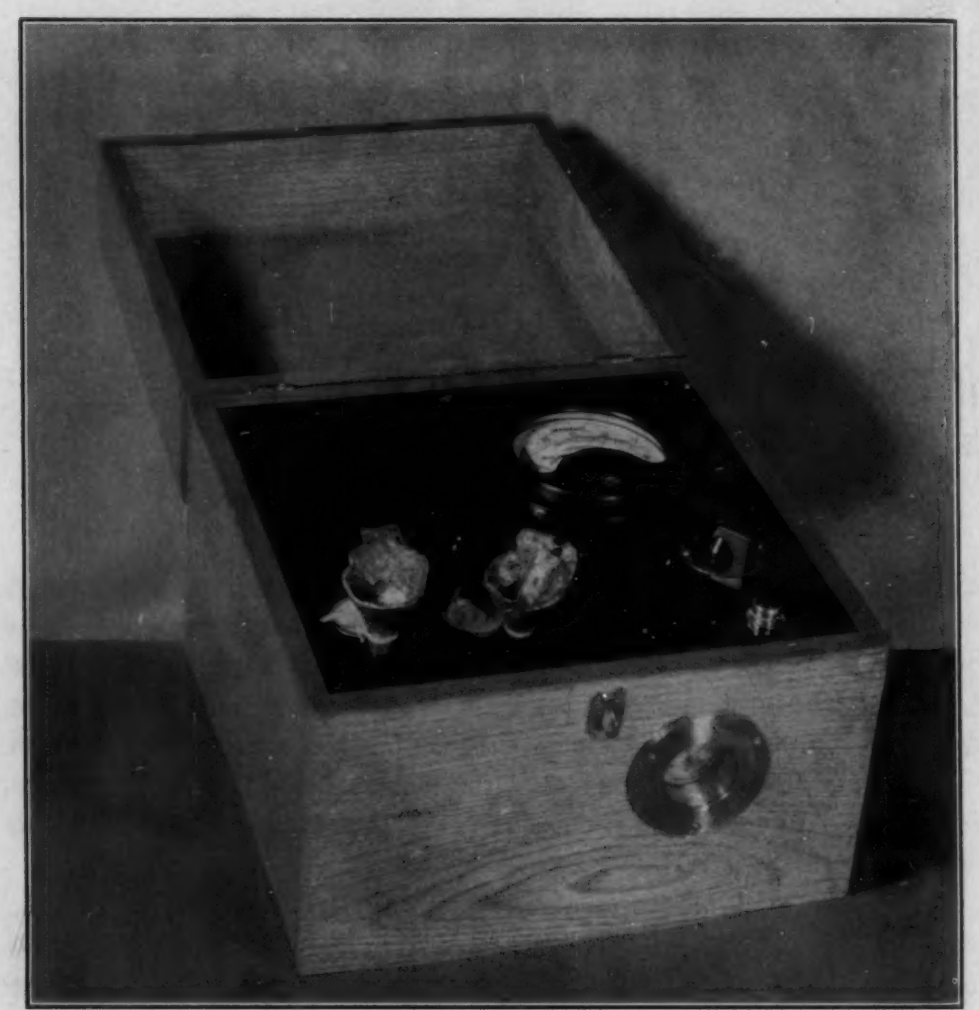

Fig. 5—The Alternating-Current Carbon Tester.

showed the advisability of using a different treatment for samples containing less than 0.35 or 0.40 per cent carbon. Therefore samples in this range were held in the mold for about 1 minute to insure that they had already passed through the critical range at a slow rate before being quenched.

A reading was taken on a sample by inserting it through the

hole in the panel into the transformer frame—that is, in the position of the right-hand sample shown in Fig. 5—and noting the reading on the meter. The operation required 20 or 30 seconds. Results were slightly more consistent when the sample was rotated slowly by hand while the reading was being taken. When tests were not in progress the standard specimen was left in the test cavity, and whenever the meter did not indicate the correct reading—the motor-generator set ran continuously—the rheostat in the primary circuit

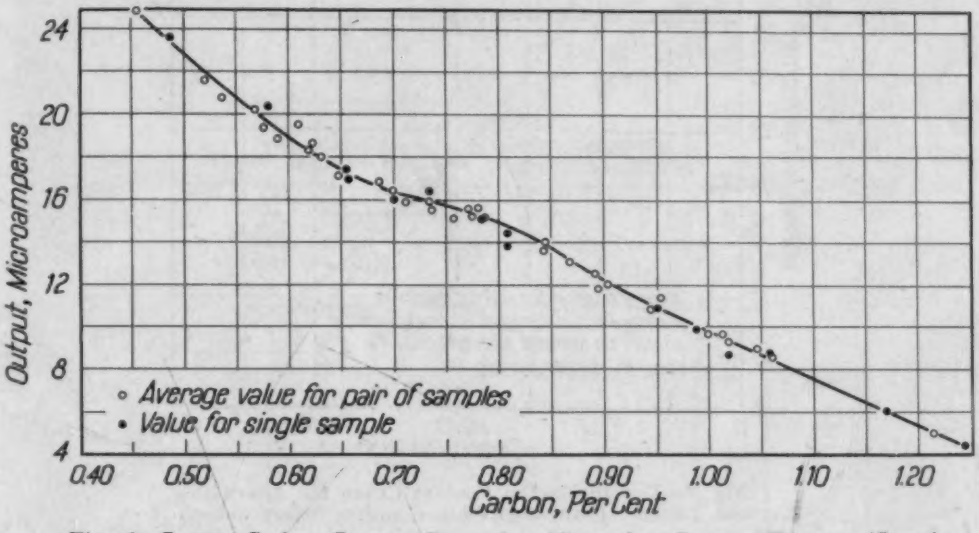

Fig. 6—Current-Carbon Content Curve for Alternating Current Tester. (Samples quenched immediately).

was moved a notch or two to make it do so. When samples that had been held in the mold for a minute were to be tested, the switch in the center of the panel was moved to cut out some of the turns of the secondary coils before the sample was inserted.

Results of Alternating-Current Measurements—The relationship between instrument reading and carbon content is exhibited graphically in Figs. 6 and 7. Fig. 6 shows the current-carbon content curve for samples quenched immediately and Fig. 7, the curve for those held 1 minute before being quenched. In both figures the average values for pairs are shown by empty circles and the points for single specimens by filled ones. Among the samples represented by Fig. 7, the agreement in carbon content between members of pairs was not very satisfactory. Pairs for which the discrepancy was greater than 0.02 per cent carbon are indicated by an x instead of a circle. Pairs which showed a divergence in excess of 0.03 per cent

were discarded. Two pairs of samples in this group were not used because the differences in the readings were excessive and another pair was not used because readings gave points so far from the curve that an error in observation was indicated. Two pairs were also discarded from the group on which Fig. 6 is based because of large

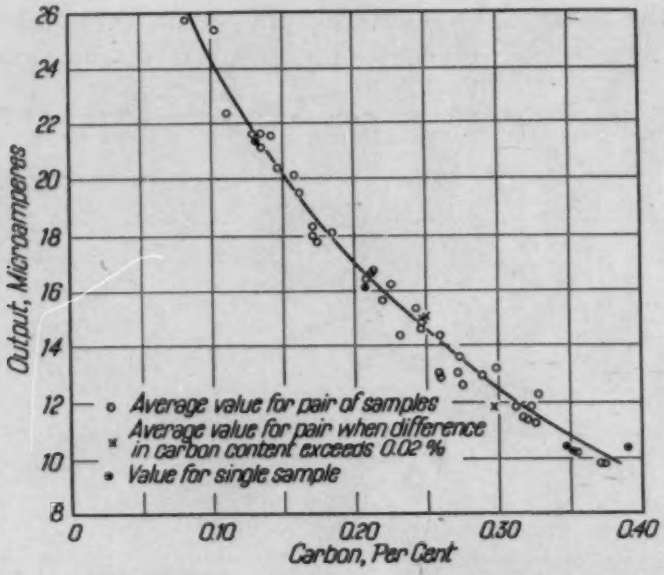

Fig. 7—Current-Carbon Content Curve for Alternating Current Tester. (Samples held one minute before quenching).

divergence between readings. Where similar discrepancies occur in practice, check samples are taken. Measurements made by the alternating-current method are influenced considerably by aging of the samples. In 2 hours the readings may change by an amount which corresponds to a loss of 3 or 4 points of carbon.

Little comment appears necessary on the character of the graphs. The correlation is not quite as satisfactory as that in the determination of carbon content by saturation measurements, but it is good enough for control work and for some purposes is sufficiently accurate for final analysis. The method is the most rapid and convenient of those described in this paper and has the advantage that the observations are made on a stationary pointer. It also has the advantage of covering virtually the entire range of carbon content, at least up to 1.10 per cent, and presumably much higher, although it requires two types of heat treatment of the samples.

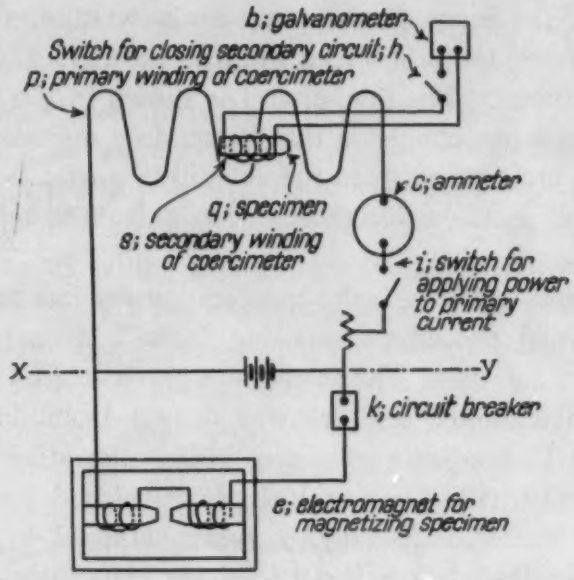

Fig. 8—Circuit Diagram of the Portable Coercimeter Test Set.

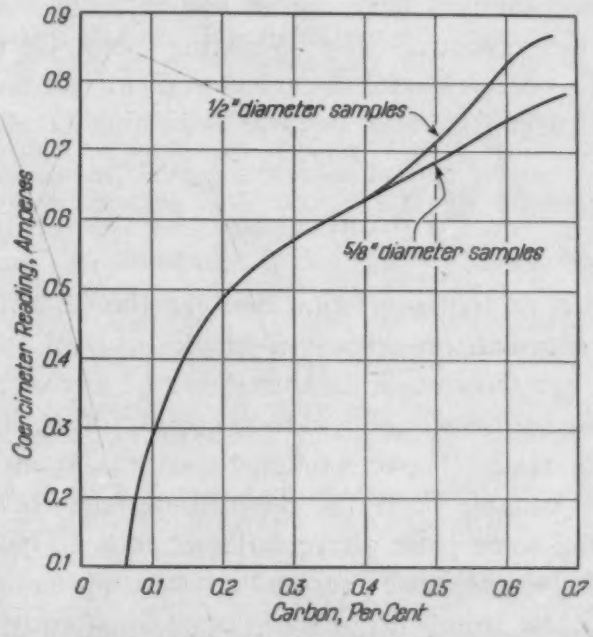

Fig. 9—Calibration Curve for ⅝-Inch Diameter and ½-Inch Diameter Steel Samples in Model B Coercimeter.

Determination of Carbon from Measurements of Coercive Force

The use of measurements of coercive force by a coercimeter (16, 17) to determine carbon content has been described in a previous

publication (15). Since that account was written, the measuring apparatus has been simplified in a number of ways and is now contained in one cabinet. The new circuit is shown in Fig. 8. It differs from the previous one chiefly in that it has only one range (two having been found unnecessary), in the substitution of a 6-volt for a 12-volt battery, and in the replacement of a galvanometer by a microammeter.

Experimental work with the new equipment has been limited to an investigation of the effect of using ½-inch diameter instead of ⅝-inch diameter samples. The results are given in Fig. 9. The curve for the ⅝-inch diameter samples was drawn from data which the Wheeling Steel Corporation obtained while calibrating their instrument at the Steubenville plant and kindly furnished for the authors' use. Data for the ½-inch samples were obtained by the authors. The figure shows that, below about 0.40 per cent carbon, samples of both sizes have about the same coercive force, whereas above this point the ½-inch samples have higher values. The reason for this divergence is not obvious. The Wheeling Steel Corporation also showed that the coercive current-carbon content curve is practically horizontal over a considerable interval beginning at about 0.70 per cent carbon.

Conclusion

Investigation of the correlation between the carbon content and three different magnetic properties of samples of steel from the open-hearth furnace has shown that measurements of any of these properties may be used for determining carbon content, at least over certain ranges. The correlation between magnetic saturation and carbon content provides a suitable basis for determining the content between 0.50 per cent and some point above 1.10 per cent. The permeability at low field strengths shows a practical relationship to the percentage of carbon from low values up to some point apparently well beyond 1.10 per cent. Two types of heat treatment are desirable in covering the entire range. The use of low frequency alternating currents to measure permeability has the advantage of giving a reading on a stationary pointer rather than by a ballistic throw. Measurements of coercive force give satisfactory information on the carbon content of samples up to about 0.70 per cent when these samples are quenched through the critical range.

ACKNOWLEDGMENTS

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DISCUSSION

Written Discussion: By K. L. Scott, engineer, Western Electric Co., Chicago.

To anyone accustomed to the perverse variations of magnetic properties of the various alloys used as magnetic materials, in which the final magnetic properties appear to depend upon every step in a long history of thermal cycles and mechanical deformation, as well as composition, it is interesting to see a definite correlation established between a single variable, such as carbon content, and any one of the measurable magnetic properties of a material. No doubt the absence of a long series of thermal and mechanical operations is what makes such a correlation possible.

The authors point out the less satisfactory correlation obtained with values from the alternating current tester than from the saturation tester. The readings from both instruments are directly proportional to the cross sectional area of the test specimens, and unless these areas are held within very close limits, the correlation will be correspondingly upset. In addition, variations in diameter of the specimens will affect the air gap between the specimen and the yoke, in the alternating current tester, which in turn will affect the readings in the same direction as the variations in area. It would be of interest to know whether the authors found any correlation between cross section of the individual test specimens and the deviations from the smooth curves.

Written Discussion: By Harold T. Clark, manager of research and development, Jones and Laughlin Steel Corp., Pittsburgh.

This paper by Dr. Rogers and his associates supplies some new and interesting information concerning the effect of carbon on several of the magnetic properties of steel. So far as the rapid determination of carbon in

steel is concerned, the Alternating Current Method apparently covers the same range of carbon content as the other magnetic methods now in use, while the useful range of the coercimeter would probably meet the needs of many open-hearth shops.

Permeability measurements of low carbon samples held in the mold for one minute are known to be different from those of similar samples quenched immediately. Since the same samples are used in the saturation tester and the alternating current machine, the latter being a form of permeameter, it would be of interest to have the answer to the following questions: (1) Is the saturation value the same for all samples under perhaps 0.35 per cent carbon regardless of heat treatment or carbon content, and (2) does a defective sample read low (or high) by the same amount by the different methods?

The accuracies of the saturation tester and the alternating current method in the higher carbon range seem comparable, while the latter, as indicated in Fig. 7 and on page 980, is not quite as accurate for carbons from 0.40 per cent down. This may be due to the difficulty of obtaining sound samples of low carbon steel or to varying rates of cooling of the sample in the mold. It is important that sufficient aluminum to completely kill the steel be used at all times and that the mold be in good condition and at the proper temperature.

Oral Discussion

S. R. WILLIAMS:[6] I should like to ask the speaker about the dimensions of the samples. They must be all equal—am I correct on that point?

Authors' Reply

To answer Mr. Scott's question, the area of cross section does make a difference and, if the sample has a seam down the side or a cavity in the center as sometimes occurs, the evidence appears in the results. With satisfactory specimens from a good mold, the variation in diameter is small and does not seem to be a source of trouble in a practical way. At least, what differences are present are masked by other effects more difficult to control.

Changes in position of the sample in the yoke also alter the readings slightly, possibly more because of inhomogeneities in the sample than on account of variations in the air gap. We found that we could get consistent readings by simply rotating the specimen in the cavity in which it was placed for test while taking the reading.

Dr. Clark asks two questions. The answer to the first is that in the range below 0.35 per cent carbon, both composition and heat treatment make a slight difference. Samples quenched through the transformation range have a slightly lower saturation value than those allowed to remain in the mold for one minute, but the difference is hardly greater than the extreme variations of individual samples in this range. We did not study accurately the alteration in saturation value with carbon content in this range because the change was obviously too small to be useful. The incidental variation among samples was as great as would be produced by, perhaps, 10 to 15 points of carbon.

[6]Professor of Physics, Amherst College, Amherst, Mass.

In answer to the second question, samples which were defective generally showed roughly comparable deviations from the calibration curves of both instruments. With carbon contents of, perhaps, 0.50 to 0.80 per cent carbon, the readings on the saturation tester appeared to be less affected by faulty technique in taking samples than were the results on the alternating current tester. With higher carbon samples, the deviations were roughly the same.

Replying to Professor Williams, yes, the saturation value and the permeability must be measured on samples that have the same dimensions. For samples cast in a given mold, the variation is surprisingly small. A slight reduction in diameter is observed as the carbon content diminishes, of the order of 0.001 inch between 1.0 and 0.40 per cent carbon. This continuous change is incorporated automatically in the calibration curves. Ordinarily, defects incidental to casting and quenching the samples are much more troublesome than variations in diameter.

NOTES ON THE INTERPRETATION OF X-RAY DIFFRACTION DIAGRAMS AND EVIDENCE OF MOSAIC STRUCTURES

By N. P. Goss

Abstract

The fundamentals of X-ray diffraction are briefly reviewed and there is shown experimentally that Laue spots may be due to

1. *Characteristic radiations,*
2. *Continuous radiations,*
3. *One and two superimposed.*

Unless good experimental technique is used it is sometimes difficult to distinguish these conditions, and therefore precaution must be exercised when interpreting X-ray diffraction diagrams.

Even though the X-ray radiation may be strongly filtered, some continuous radiation having wavelengths close to the characteristic radiation will be strongly transmitted. When such radiation is diffracted by the atomic crystal planes, in accordance with Bragg's law, the Laue spots will appear elongated, and even diffuse or ill-defined. This condition is due only to the superimposing of the continuous and characteristic radiations, which differ but slightly in wavelength from each other.

X-ray evidence is also presented to show that grains are essentially mosaic in annealed metals, that is, built up of crystal units smaller than the grains and differing slightly in orientation.

WHEN X-rays are generated in an X-ray tube, two types of radiation are emitted—characteristic and continuous. The characteristic radiation is as its name implies characteristic of the target element and is only emitted when the impressed voltage reaches a critical potential. To excite the characteristic radiation from a molybdenum target about 19,000 volts is required, but an intense supply is only obtained when a voltage of 30,000 to 40,000

A paper presented before the Twenty-second Annual Convention of the Society held in Cleveland, October 21 to 26, 1940. The author, N. P. Goss, was physicist, Cold Metal Process Co., Youngstown, Ohio, now research engineer, American Steel & Wire Co., Cleveland. Manuscript received June 20, 1940.

is applied to the X-ray tube. The characteristic radiation has a definite wavelength and for metallographic diffraction work the $K\alpha$ and $K\beta$ are used. The $K\alpha$ radiation actually consists of two wavelengths differing only slightly from each other and are called $K\alpha_1$, and $K\alpha_2$ or the $K\alpha$ doublet.

Table I presents a list of characteristic $K\alpha$ and $K\beta$ radiations emitted from various elements most frequently used in metal-

Table I

Atomic Number	Element	$K\alpha_2$ Line	$K\alpha_1$ Line	$K\beta$ Line	Filter or Screen
		A.U. 10^{-8} cm.			
42	Molybdenum	0.7121	0.7078	0.6315	Zirconium
29	Copper	1.5412	1.5374	1.3893	Nickel
28	Nickel	1.6583	1.6545	1.4970	Cobalt
26	Iron	1.9360	1.9321	1.7530	Manganese
24	Chromium	2.2889	2.2850	2.0806	Vanadium
27	Cobalt	1.7892	1.7853	1.6174	Iron

lographic work. Sometimes it is desirable when studying complex alloys to eliminate the $K\beta$ line, and this greatly simplifies the spectrum. Table I also gives a list of elements used as filters which will

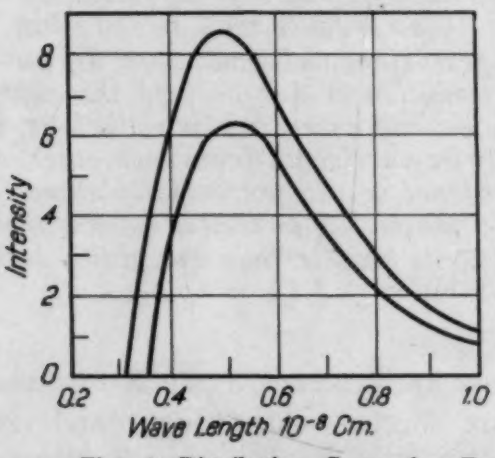

Fig. 1—Distribution Curve for Two Tube Potentials Most Commonly Used in Diffraction Work.

practically eliminate the $K\beta$ line. A filter, usually 0.005 to 0.010 inch thick, will reduce the intensity of the $K\beta$ line to such an extent that for average exposures it will be entirely eliminated. However, for most X-ray work the elimination of the $K\beta$ line is not required.

The continuous, or white radiation, is a band spectrum and varies over a considerable range of wavelengths and of varying

intensity depending upon the voltage applied to the X-ray tube. Fig. 1 gives the distribution curve for two tube potentials most commonly used in diffraction work.

This curve shows that the continuous radiation is most intensely emitted in the band of wavelengths ranging from about 0.4 to 0.6 Ångström units (10^{-8} cm).

The continuous radiation is created when the electron beam strikes the target, and the wavelength depends only upon the velocity the electrons have attained at the time of impact on the target. If the electron beam consists of a beam of electrons moving with substantially the same velocity and uniform collision with the atoms of the target, only one wavelength will be emitted, or at most a very narrow band of wavelengths.[1]

The radiation emitted by an X-ray tube therefore consists of two types of radiation—continuous and characteristic.

To determine the wavelength of the characteristic and continuous radiations a single crystal of known lattice dimensions is used. By setting the crystal at various angles to the X-ray beam and taking a series of spectrograms the wavelengths can be calculated by using Bragg's law—$N\lambda = 2\ d\ \mathrm{Sin}\ \Theta$.

When a perfect single crystal is used the wave lengths can be sharply separated. However, when the crystal is imperfect, or mosaic, this is no longer possible.

In annealed metals the crystals are never perfect. This means that the grains actually consist of many small lattice blocks slightly displaced relative to each other. It seems that these are of the order of 10^{-5} cm and larger.

A mosaic crystal set to reflect the characteristic radiation, when examined by the Laue method, will also be in a position to reflect any wavelengths which differ slightly from the characteristic radiation. Some general radiation will always be present to satisfy this condition. Therefore, if the Laue diagram of a fine-grained specimen of low carbon strip steel is examined by the Laue method one will find that many of the diffraction spots are due to the reflection of characteristic and continuous radiation from the mosaic crystals.

Interpretation of X-Ray Diagrams

The pinhole diagrams shown in Fig. 2 were made with molyb-

[1]See discussion by Carapella. He pointed out that even electrons having the same velocity would on striking the target emit radiations of various wavelength.

denum and cobalt radiation using the same specimen. The pinholes were 0.020 inch in diameter and spaced 9 centimeters apart. On close examination many of the pinhole spots were found to be due to the reflection of the continuous and characteristic radiation from the atom planes. Some are due entirely to continuous radiation and others are due to characteristic radiation (especially in the higher order lines).

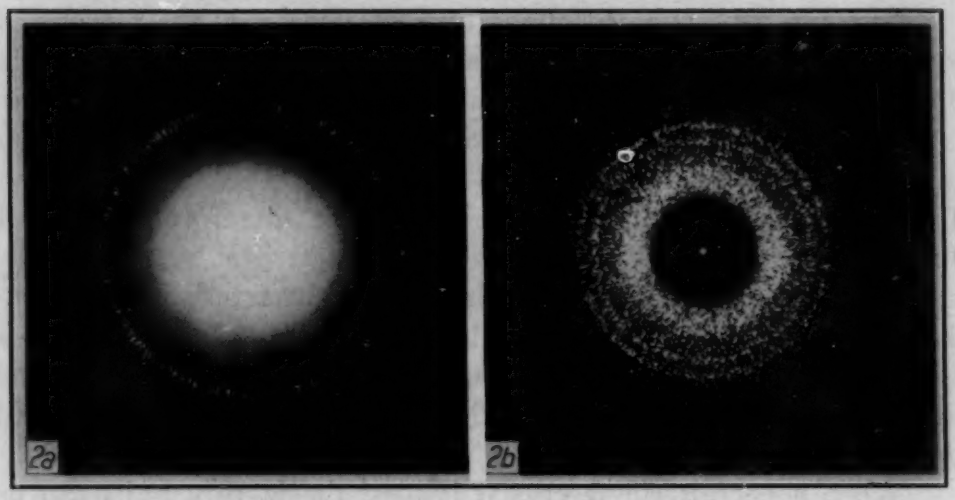

Fig. 2—Annealed Ingot Iron. (a) Cobalt Radiation, Fe Filter; (b) Molybdenum Radiation, no Filter.
The X-Ray Beam was Transmitted Through a Section Approximately 0.005 Inch Thick.

From an examination of the distribution curve of the continuous radiation it can be seen that the greatest intensity should be due to crystal planes reflecting X-rays having wavelengths in the range 0.4 to 0.7 Ångströms.

The pinhole diagram made with the cobalt radiation is of unusual interest; only one ring is present while in the one made with the molybdenum radiation, using the same specimen, many rings are present.

The structure of the radial streaks of the pattern made with the cobalt radiation is also of interest. Each streak has a very definite structure—several pairs of strong lines close together are due to the $K\alpha$ doublet; and the elongated streaks superimposed are due to continuous radiation. Such an X-ray structure can only be attributed to the mosaic texture of the grains. It should also be pointed out that the specimen for X-ray examination was prepared before heat treating. The specimen used was ingot iron, cold-rolled to 0.005 inch and

annealed at 1335 degrees Fahr. (725 degrees Cent.) for 25 minutes and cooled slowly in the furnace.

To prove even more conclusively that the grains in an annealed metal are mosaic the X-ray surface diffraction method using the following technique was employed.

A specimen of ingot iron 0.010 inch thick and annealed at 1500 degrees Fahr. (815 degrees Cent.) was placed in the specimen hold-

Fig. 3—Annealed Ingot Iron. (a) Angle of Incidence—25° 3′; (b) Angle of Incidence—25° 8′. Molybdenum Radiation, Zirconium Filter. Exposure 390 M.A. Hours. The Rectangles Shown Above Enclose Diffraction Spots for the Same Grain Which is Mosaic.

er of a surface diffraction cassette and set at an angle of 25 degrees 3 minutes to the X-ray beam (a beam of small divergence was used). The X-ray film was exposed 24 hours. After the exposure was completed the specimen was rotated 5 minutes and another exposure taken under the same conditions. These X-ray diagrams are shown in Fig. 3. If the grains are mosaic then the diffraction patterns should be substantially the same. The two X-ray films were matched and all of the diffraction spots coincided, but the intensity and the shape of the diffraction spots varied. This proves that the grains are definitely mosaic. It is reasonable to assume that perfect grains re-

flecting the X-ray beam under these conditions would have produced distinctly different X-ray diffraction patterns.

X-ray surface diffraction methods can therefore be applied to the study of mosaic or sub-boundary structures in annealed metals.

Finally, the observed diffuseness of the pinhole spots made of the annealed metals is due to the continuous radiation being superimposed on the reflected characteristic radiation. This has often been interpreted to indicate lattice distortion.

Sharper diffraction spots and sharply resolved $K\alpha$ doublets can only be obtained when the X-ray beam is substantially parallel. The longer the slit system the more parallel the X-ray beam will be. On the other hand, diffuse diffraction spots are always obtained when a divergent beam is used in the pinhole system method as well as the surface diffraction method.

This paper is presented principally to promote discussion on the matter of X-ray technique and its relationship to the structure of X-ray diffraction effects. The importance of X-ray technique is often overlooked in most X-ray metallographic work; in fact, it is usually entirely neglected, or taken for granted.

The writer believes that X-ray techinque and its effect on the X-ray diffraction diagram still remains a first class problem and that standardization of technique is in order.

This can be accomplished by organizing a symposium, the aims of which will be to standardize X-ray technique, procedure of examination, equipment and interpretation. These will be subject to change as better methods and further advances are made in the application of X-ray metallography to metallurgical problems.

DISCUSSION

Written Discussion: By Louis A. Carapella, Gordon McKay Teaching Fellow in X-Ray Metallography, Laboratory of Physical Metallurgy, Harvard University, Cambridge, Mass.

The author should be complimented for his keen interest in applying X-ray diffraction methods, particularly to the study of metals as shown by this paper. There are, however, several factors therein which are questionable, and I should like to point out and discuss them more completely.

First of all, it is doubtful as to whether the author has proved conclusively by the X-ray surface diffraction method that the annealed ingot iron used by him possesses grains of mosaic character. Results of his experiment show the diffraction markings to persist after a rotation of 5 minutes of arc.

It follows then that the angle of incidence of the diffracted beam to the planes in question did not vary. This may be due to the presence of mosaic structures, as assumed by the author, but may also be caused by the divergence of the X-ray beam, even in the presence or *absence* of mosaic structures. The author does not discuss this point. In the usual experimental set up, such as the one described by him in another paper,[1] this divergence in the most favorable case, amounts to more than 8 minutes of arc. The calculation is given below:

$$\tan\left(\frac{\delta}{2}\right) = \frac{0.010''}{2 \times 4''} = 0.00125$$

where: $\delta = 2\ (4.3') = 8.6'$ (angle of divergence).

In the above example, the grains are assumed to be so small in size that the divergence of the X-ray beam is determined chiefly by the width of the first slit as shown in Fig. A by the lines AB and BC. It is obvious, furthermore, that the divergence can vary, as the grain size is increased, approach-

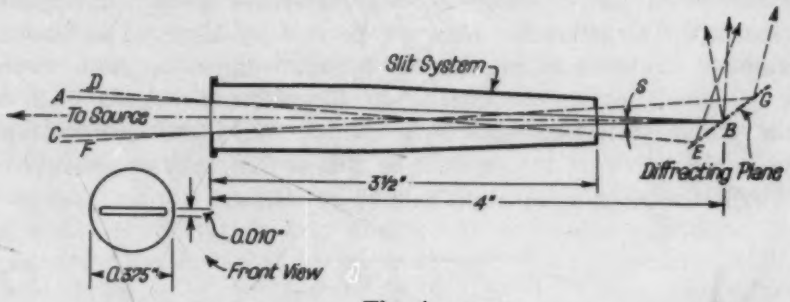

Fig. A

ing a maximum condition as indicated by the broken lines DE and FG. The divergence produced by the length of the slit, on the other hand, is somewhat greater, and so its contribution magnifies the total effect of divergence. In the absence of any demonstration in the paper regarding this factor, the author cannot be said to have proved the presence of mosaic structure from his interpretation of the X-ray photograms illustrated in Fig. 3a and 3b, unless he can show the divergence is considerably less than 5 minutes of arc.

The X-ray diagrams illustrated in Fig. 2 are generally called "pinhole-patterns"[2, 3, 4] and not "Laue diagrams"; and the method by which they are produced is known as the "pinhole method." In general, the apparatus used in the pinhole method is much the same as that of the Laue method, except the specimens are polycrystalline, and the radiation is not purely continuous but contains the strong characteristic emissions. This distinction should be emphasized, otherwise the terminology is rendered misleading.

It is very difficult to believe from Fig. 2a that a resolved $K\alpha$ doublet

[1]N. P. Goss, "Study of Lattice Distortion in Plastically Deformed Alpha Iron," American Institute of Mining and Metallurgical Engineers, *Metals Technology*, T.P. 1218, August, 1940.

[2]C. S. Barrett, American Society for Metals *Metals Handbook*, 1939, p. 190-191.

[3]G. L. Clark, "Applied X-Rays," McGraw-Hill Book Co., New York, 1940.

[4]American Society for Testing Materials, "Symposium on Radiography and X-Ray Diffraction Methods," 1936.

is actually visible, when, in fact, the resolution at such an angle for cobalt radiation is indeed small, and under ideal conditions amounts to:

$$\Theta\alpha - \Theta\alpha = 4.0'$$

Therefore, the pairs of strong lines which the author mentions must be ascribed to some source other than the $K\alpha$ doublet.

In his review on the fundamentals of X-ray diffraction, the author maintains that the wavelengths of the continuous radiation depend *entirely* upon the velocity attained by cathode electrons at the moment of impact on the target; and that, if these electrons were made to move all at the same velocity, only one wavelength would be emitted. Hence, from this viewpoint, the continuous radiation results only from the impact of electrons having different initial velocities. This, in general, is contrary to observations made on the nature of the X-ray spectrum.[5] As a matter of fact, the velocity of cathode electrons (material particles) is determined by the potential drop across the tube; and so, for a fixed voltage, there will be a constant velocity for each electron ejected from the cathode. The resulting wavelengths, however, depend primarily on the efficiency with which these cathode electrons collide with atoms in the target rather than on the velocity alone. The kinetic energy of the cathode electrons at moment of impact is given as $V_o e$, where V_o is the tube potential, and e the charge on the electron. As a collision takes place, the cathode electron suffers a change in kinetic energy represented by Ve, where $V < V_o$. It can then be shown that such a collision will give rise to a radiation of a wavelength related as follows:

$$\lambda = \frac{hc}{(V_o - V)\, e}$$

when h is Planck's constant, and c is the spread of light. If upon the first collision all energy of the cathode electron is imparted to the target atom, then $Ve = o$, and $\lambda = \frac{hc}{V_o e}$, which corresponds to the short wavelength limit. On the other hand, if the electron glances off the atom suffering little loss in energy, such that $Ve = V_o e$, then $\lambda = \infty$. The above expression is, therefore, in accordance with the curves shown in Fig. 1.

Written Discussion: By L. Thomassen, associate professor, department of chemical and metallurgical engineering, University of Michigan, Ann Arbor, Mich.

Without trying to touch on all the doubtful questions treated in this paper, the writer would like to discuss one of its main issues, namely, the so-called proofs given of the mosaic structure.

Discussing Fig. 2a, Mr. Goss makes the sweeping statement that the observed structure can only be due to the mosaic structure of the grains. Could it not just as well be produced by the reflection of separate grains? These might have almost the same orientation with regard to the X-ray beam and therefore almost overlap. (An attempt might have been made to roughly correlate the actual microscopic grain size and the lengths of the X-ray reflections estimated by geometrical considerations.)

[5] A. H. Compton and S. K. Allison, "X-Rays in Theory and Experiment," D. van Nostrand Co., New York, 1934, p. 38-40.

With regard to the second so-called proof, the rotating of the specimen five minutes and the appearance of a new reflection can easily be explained by the same assumption of reflection from separate grains. When the specimen is shifted five minutes, a new grain can easily come in such a position that it can reflect and thus be recorded. In an unpublished investigation by D. M. McCutcheon and the writer, brass samples in the form of beams were stressed without changing the relation of the point of reflection of the sample to the X-ray beam. It was observed that new reflections occurred due to slight rotation of grains by the bending, so that the Bragg relation would be satisfied.

It would therefore seem that the present article does not make any contribution to the question of mosaic structure.

Oral Discussion

G. L. CLARK:[6] I think this is a subject very much worthwhile and in general I heartily agree with the recommendations which Mr. Goss has suggested. I have known him for a long time. I know how important these details have always been in his work, and for this reason I think his work in general can be depended upon.

It certainly is true that we do need some common basis of interpretation. We have gone just as far as we can go in many ways, trying to reproduce each other's results and trying to understand published diffraction patterns, but we are far from realizing the fullest possibilities. Now this is illustrated by the fact that in the past year there have been at least nine papers that I know of, besides the lecture by Professor Debye at Cincinnati at the meeting of the American Chemical Society last spring, on anomalous effects in X-ray patterns. It has come to the fore that certain unpredicted spots on patterns, and especially those for certain metals when temperatures are raised, are always more diffuse than in the normal ones, all sorts of explanations are being submitted. Preston's idea is that a community group of an atom and 12 equidistant neighbors in a crystal is a sort of a submosaic in a sense, so that the central atom with this little family around it somehow vibrates, particularly when the heat was added, and thus produce an anomalous spot.

Professor Zachariasen of Chicago, and Raman in India, have contributed also to this field. There have been a number of papers on anomalous spots in graphite blacks, and other materials, just to show how interested people are in really getting every drop of information out of these patterns. Diffraction patterns are just as wonderful to me today as they were 18 years ago, because every specimen is an entirely new experience in itself. We cannot predict much of anything about the results with a given specimen. It is for this reason particularly that we must understand our physics very perfectly—the physics of X-rays, the production of X-rays, the measurement of wavelengths and the spectrum we are using. We must understand the physics of our radiation before we can begin to understand and

[6] Professor of chemistry, University of Illinois, Urbana, Ill.

make full use of the results of an inter-action between an invisible radiation and a certain complicated architectural arrangement.

So I think that a suitable committee might well consider this particular problem of technique, at least in the matter of reproducing results. Possibly we ought to have a series of specimens and have different laboratories make patterns of the same specimens, just as a few years ago, you will remember, 22 different people or laboratories made the A.S.T.M. standard photomicrographs for grain size determinations. Maybe this is the time to adopt a similar method, leading to increased co-operation in this science in the first place. Coming out of it will be, I am sure, great good.

The number actually doing this diffraction work is limited. As Mr. Goss indicated, it is a specialized technique and it takes years to learn how to do it adequately. I am sure none of us who do X-ray work would say that we knew everything about what we are working with. I think it is the experience of all of us, Dr. Mehl and Dr. Hanawalt and myself, and others, that the more we know about this wonderful field the less we know about it.

R. F. MEHL:[7] I have been thinking a bit since Mr. Goss made his suggestion of a symposium to consider the adoption of standard methods in X-ray technique. Although I am relying upon my memory, I believe that the American Chemical Society has an active committee engaged in somewhat similar work, and I think that one of the physical journals is intending to bring out a volume on X-ray methods that might be of use in this connection also. Of course the A.S.T.M. committee on X-ray diffraction is still very active and might very well consider the proposal that Mr. Goss makes.

Author's Reply

The remarks of Professor Clark are certainly appreciated. I am sure that everyone recognizes the many contributions he has made in applying X-ray diffraction methods to industrial and scientific problems. Without question his enthusiasm and love for his work have in no small measure kept this science alive in our country.

His suggestion that some committee be organized to send a group of specimens to various X-ray laboratories for examination is a splendid idea. When this work has been completed a symposium on X-ray technique can be organized and the results compared. The methods which yield the best X-ray diffraction diagrams and the most information should then be adopted as standards by convention. This in a sense would be similar to the standardization of microscopic technique. It is quite obvious that the X-ray technique and interpretation of X-ray diffraction diagrams must be standardized, for without standardization of technique results from different laboratories cannot be compared directly and the chances are that they may even be contradictory.

Likewise Dr. Mehl's laboratory has enriched the field of X-ray metallography, especially in theoretical metallurgy.

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[7]Director, metals research laboratory, and head, department of metallurgy, Carnegie Institute of Technology, Pittsburgh.

Mr. Carapella and Professor Thomassen question whether I have proved conclusively the existence of mosaic structure of the grains examined in this paper. In this short paper it was hardly possible to present sufficient data, for it was assumed that most grains in metals have sub-boundary[8] structure and that the X-ray can easily detect such structures.

Mr. Carapella points out that the divergence of the X-ray beam must be considered, especially when the settings of the specimen differ but slightly from each other. He has calculated the divergence from the dimensions of the slit system presented in another paper. The author has checked this experimentally and has found that the divergence of the X-ray beam was less than 8 minutes. In addition to the divergence, the size and perfection of the diffracting crystal must also be taken into consideration.

(Experimental studies made in my laboratory indicate that a large crystal seems to be more sensitive to divergence than a small crystal. Also, the structure of the $K\alpha$ doublet lines is greatly affected by the size and perfection of the crystals.)

Now, according to the calculation made by Mr. Carapella, a rotation of 5 minutes does not necessarily prove the existence of a mosaic structure because the divergence of the beam is about 8 minutes and, therefore, the crystal would reflect strongly in both positions. He is quite right in considering such a possibility. It is therefore necessary to show that the position of the $K\alpha$ doublet remains unchanged when the rotation of the specimen is in excess of 8 minutes. Therefore, if the diffraction spots remain in the same position the grain must be mosaic. To meet these objections raised by Mr. Carapella and Professor Thomassen, the author has reproduced the entire series of X-ray diagrams made of a specimen similar to the one shown in Fig. 3, although the grains were slightly larger. These surface diffraction diagrams are reproduced in Fig. 4. In Fig. 4a the angle of incidence was 24 degrees 57 minutes. One can observe that doublets are clearly resolved; this can be due either to the divergent X-ray beam being reflected from the surface of a perfect crystal or it may indicate a mosaic structure. For the next exposure the specimen was rotated 10 minutes of arc, which is slightly in excess of the divergence factor. The angle of incidence was now 25 degrees 7 minutes. The position of most of the diffraction spots remain unaltered after a rotation of 10 minutes of arc, and the resulting X-ray diagram is shown in Fig. 4b. The doublet enclosed in the rectangle was found to be in exactly the same position.

In Figs. 4c and 4d the specimen was set at 25 degrees 15 seconds and 25 degrees 24 minutes respectively and the position of the $K\alpha$ doublet and its structure in general remain unaltered, though the doublet in Fig. 4d is of reduced intensity (enclosed in rectangle). The total angular rotation of this crystal face was about 27 minutes, which is far in excess of the divergence of the X-ray beam. This grain is therefore mosaic and the block displacement is quite large.

To prove to Professor Thomassen that these diffraction effects are not due to separate grains, as he suggests, but actually due to the mosaic struc-

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[8]N. P. Goss, "Sub-boundary Structures of Recrystallized Iron," Technical Paper No. 1236, American Institute of Mining and Metallurgical Engineers.

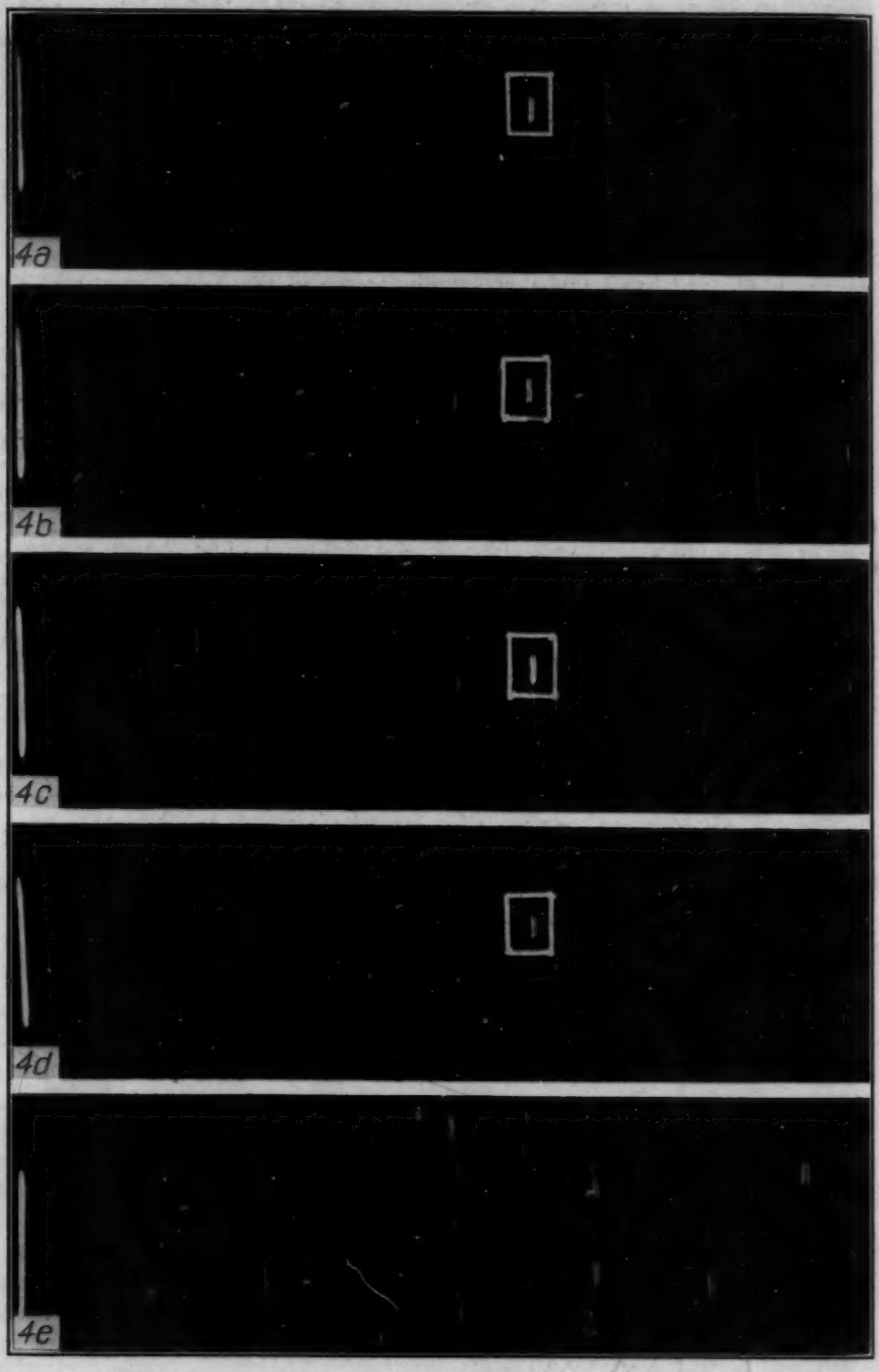

Fig. 4—Annealed Ingot Iron. Fig. 4d Shifted to Make Fig. 4e.

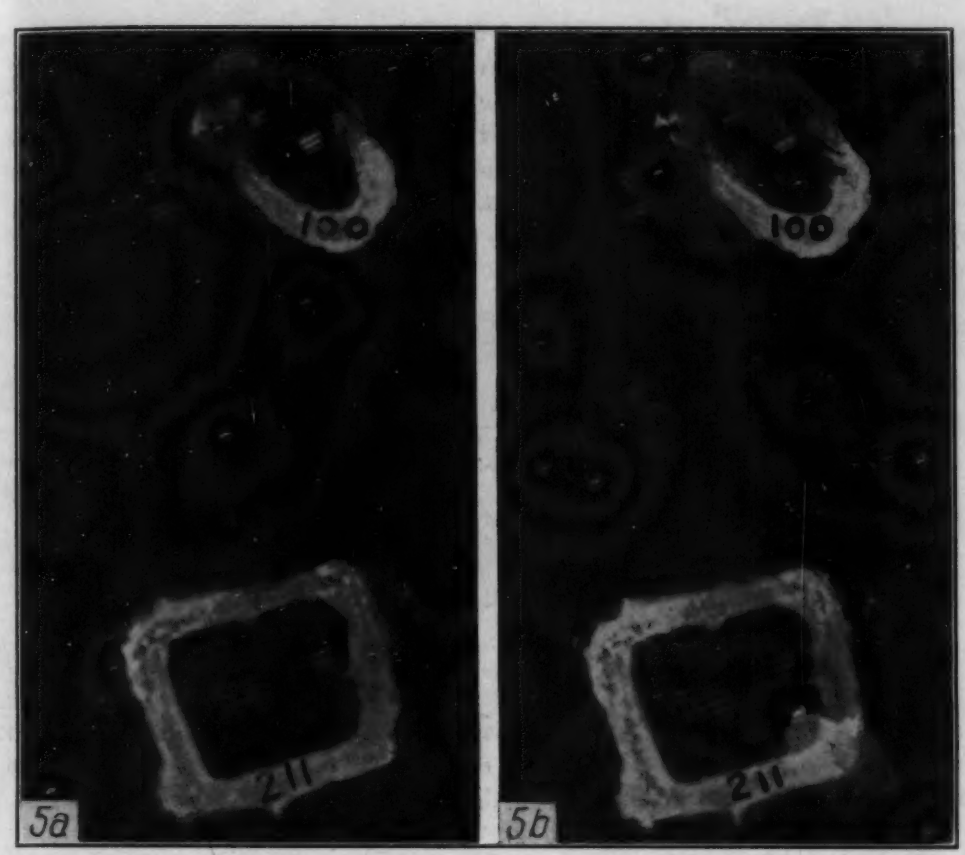

Fig. 5a and b—Enlargements of X-rays. × 6.
Fig. 5a—Emulsion Removed from One Side of 211; Emulsion on Both Sides of 100.
Fig. 5b—Emulsion Removed from One Side of 100.

ture of the grains, the following procedure was followed: The specimen was shifted slightly in the specimen holder, but the same angular setting of 25 degrees 24 minutes was maintained. This shifting should cause the X-ray beam to strike a new set of grains and therefore diffract the $K\alpha$ radiation to new positions on the X-ray film. The diffraction pattern resulting is shown in Fig. 4e; this pattern is obviously entirely different from the one shown in Fig. 4d and therefore due to an entirely new set of grains.

Mr. Carapella also points out that one should not expect to find resolved $K\alpha$ doublets on pinhole diagrams. This certainly is true when an X-ray beam of large divergence is used. In the pinhole diagrams shown in the paper a pinhole system was used in which the pinholes are spaced 9 to 22 centimeters apart. This is done to secure a fairly parallel beam of X-rays. This, however, reduces the intensity of the X-ray beam to such an extent that long exposures are required (as long as 72 hours).

It is suggested that the strong pairs of lines are due to some other cause. It is admitted that many of these double spots are due to double emulsion; for if the emulsion is removed on one side of the film one of the lines disappear. This is not true of all the double pairs; if the spots are carefully examined with a low power magnifying glass one can find spots which con-

sist of three lines close together and equally spaced, and of about the same intensity. If the emulsion is removed from one side of the film only two lines are found to remain and one of these is usually of less intensity than the other. The reason for this is that the double separation and the spacing of the lines due to the double emulsion is about the same for the experimental set-up. To avoid this difficulty a single emulsion film should be used.

Figs. 5a and 5b are enlargements made of an X-ray diagram (pinhole method) to show the $K\alpha_1$ and $K\alpha_2$ lines. These enlargements were enlarged

Fig. 6—Annealed Ingot Iron.

about six times to show the doublets in greater detail. It is well to state at this time that making enlargements is not standard practice but was adopted as a means to prove the points under discussion. Each enlargement has two areas enclosed, one being an oval and the other a square.

Before making the enlargements, the emulsion had been removed from one side of the film. The square area is located in that area and shows the doublet lines very strongly; it also shows the clarity and detail obtained with our X-ray equipment.

The area covered by the oval was not touched and the enlargement, Fig. 5a, was made. If closely examined, one can see three strong lines in the center of the oval and two lines of equal intensity in the upper portion of the oval. The emulsion was removed in the oval (the scratches can be seen) with a razor blade and another enlargement, Fig. 5b, made. Looking first in the center of the oval, one notices that instead of three lines there are now only two. The doublet remains, proving that the third line was due to the double emulsion. In the upper portion of the oval the two lines persist but the intensity varies in a ratio of two to one. This ratio is to be expected of the $K\alpha$ doublets under certain conditions.

It should be understood that the pinhole method is not as accurate as the surface diffraction method. The surface diffraction method gives greater detail and does not offer the double emulsion difficulty since the diffracted rays are always perpendicular to the film surface.

We have good experimental evidence that a crystal can diffract only one of the doublet lines when a substantially parallel beam of X-rays is used.

Fig. 6 shows a surface diffraction diagram in which one or the other of the doublet lines is missing. A rectangle is drawn about such a doublet line. A large number of surface diffraction diagrams have been made of

annealed metals in which the diffraction spots (doublets) appear diffuse and ill defined, and which is believed to indicate a mosaic structure in which the block displacements are very small; in other words, the structure of the doublet lines is even a more sensitive indicator of mosaic structures.

Likewise, many of the lines which appear only as single lines in the X-ray diagrams made with a pinhole system either are K_1 or K_2 lines. Some of these lines are also due to the continuous radiation, though such diffraction spots usually appear as radial streaks, or have greater width.

It is hoped that this paper and the enlightening discussion presented will stimulate further work along these lines. This will extend the use of diffraction methods and improve the X-ray technique.

FREE-CONVECTION COOLING OF MILD STEEL BARS AND RODS—GRAPHICAL TIME-TEMPERATURE RELATIONS

By John Griswold and O. S. Jenkins

Abstract

Charts are presented by which the time required for hot iron rods, tubes, and bars to cool in air can be quickly determined. The method was developed by graphical integration of an equation for simultaneous heat loss due to radiation and natural convection.

A number of graphical integrations of this equation were made, covering the usual ranges of the variables. Experimental cooling curves are closely represented in terms of a calculated curve for a "unit bar" by the relation

$$\Theta = (W/A)(M)(\Theta_o)$$

Θ_o is the time for cooling of the unit bar from T_1 to T_2 as read from a chart. (W/A) is the weight to surface area ratio. M is a multiplier which corrects for differences in the convection coefficient, and in the radiation angle and emissivity factors between any given bar and the unit bar.

A nomograph and charts are presented for evaluation of this multiplier and its component variables for temperatures up to 1650 degrees Fahr. (900 degrees Cent.). The method while developed and tested for iron and soft steel appears to be applicable to high carbon steel also except for narrow temperature ranges around 1200 degrees Fahr. (650 degrees Cent.).

MANUFACTURE of iron and steel articles frequently includes hot working operations, heat treatment, case hardening and other processes which must be conducted at elevated temperatures. In the case of heat treatment, the articles must be heated and cooled to exact temperatures. Elsewhere, the pieces must be cold for some other step following a hot process. Hence a rapid and accurate means of determining time requirements for metal bars to cool from

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one temperature to another is needed. Such a method has been developed for iron and mild steel by first making a number of graphical integrations for heat loss through simultaneous radiation and natural convection, then correlating the results by a factor which includes shape, size, and radiation variables. Although exact factors for convection coefficients are not available for shapes other than rounds, they can be satisfactorily approximated. Experimental cooling curves taken on a number of shapes closely fitted calculated curves.

Development of Simplified Relations

Take the case of a single bar cooling in air. The rate of heat loss at any moment by radiation and natural convection (neglecting a small temperature difference from center to surface) is (6)[1]

$$dQ/d\Theta = (W)(C)(dT)/(d\Theta) = A(h_c + h_r)(T - T_r) \qquad (a)$$

W is the weight, C is the specific heat, A is the surface area, h_c is the coefficient of natural convection, h_r is the radiation coefficient, T is the temperature of the bar, and T_r is the temperature of the surrounding air. The major variables are T, Θ, and h_r; the minor variables are C and h_c.

The convection coefficient is correlated by the following relation (4):

$$h_c = \frac{k_c}{(D')^{0.25}} (T - T_r)^{0.25} \qquad (b)$$

k_c is a constant and D′ is the diameter of a round bar (in inches). For a bar of any given cross section, this may be written

$$h_c = a\,(T - T_r)^{0.25} \qquad (c)$$

in which a is a constant depending upon the size and shape of the bar.

The relation for the radiation coefficient is (5)

$$h_r = \frac{0.173\,(T^4 - T_r^4)\,F_A F_E}{10^8\,(T - T_r)} \qquad (d)$$

F_A and F_E are radiation angle and emissivity factors, respectively. Defining K by the relation,

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

$$K = \frac{10^9}{0.173\, F_A F_E} \qquad (e)$$

equation (d) may be written

$$h_r = \frac{(T^4 - T_r^4)}{K\,(T - T_r)} \qquad (f)$$

Combining equations (a), (c), and (f), and solving for $d\Theta$ gives:

$$d\Theta = \frac{(W/A)\, C\, dT}{a(T - T_r)^{1.25} + (1/K)(T^4 - T_r^4)} \qquad (g)$$

Over a temperature range, K varies with F_E, but the latter changes so slowly that an average value may be used without appreciable error. The expression for the time of cooling from T_1 to T_2 is obtained by integrating equation (g)

$$\Theta = K\,(W/A) \int_{T_2}^{T_1} \frac{C\, dT}{T^4 + K\, a\, (T - T_r)^{1.25} - T_r^4} \qquad (h)$$

Graphical integration of the right-hand member of equation (h) for a "unit bar" (W/A = 1.0) at three air temperatures—T_r = 60, 100 and 120 degrees Fahr.—gave the curves of Fig. 1 for temperature T against time Θ. In this calculation, a was taken as 0.5, and $F_A F_E$ was taken as 1.0. The specific heat data for iron reported by Austin (1) were used.

Having Fig. 1, the time of cooling of any other bar between the same temperatures may be expressed by the relation

$$\Theta = (W/A)\, M\, \Theta_o \qquad (i)$$

in which Θ_o is the time of cooling of the unit bar read from Fig. 1, and M is a multiplier which depends upon the size, shape, radiation emissivity, and angle factors of the bar in question. By its definition, this multiplier is

$$M = \frac{\Theta}{(W/A)(\Theta_o)} = (1/\Theta_o) \int_{T_2}^{T_1} \frac{C\, dT}{T^4 + K\, a\, (T - T_r)^{1.25} - T_r^4} \qquad (j)$$

The results of a number of graphical integrations of equation (j) over usual ranges of $F_A F_E$ and a, at the three air temperatures noted, are presented as the nomographic chart, Fig. 2, from which the value of M is readily determined.

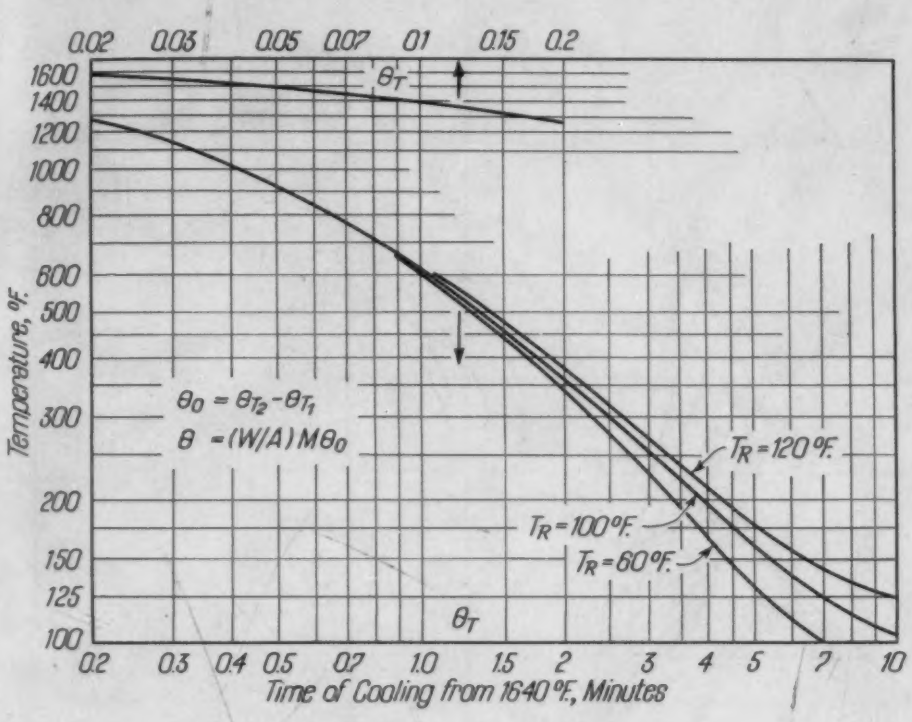

Fig. 1—Cooling Curve for Unit Bar.

M is not a constant, yet it varies only slowly with temperature. usually falling between 1.0 and 2.0 as may be seen from Fig. 2. For use over a temperature range, M is determined at the temperature existing at the *mid-time interval for the unit bar,* read from Fig. 1. This means that the proper value of M is found at a lower temperature than the arithmetic average.

Experimental Verification

Cooling curves were determined by a potentiometer and calibrated iron-constantan thermocouple, on ten soft steel bars and one eutectoid steel bar. The bars were 18 to 30 inches long and were insulated on the ends. They were supported in a horizontal position, while cooling, by two thin, vertical, notched, transite plates, which interfered with radiation and natural convection only slightly.

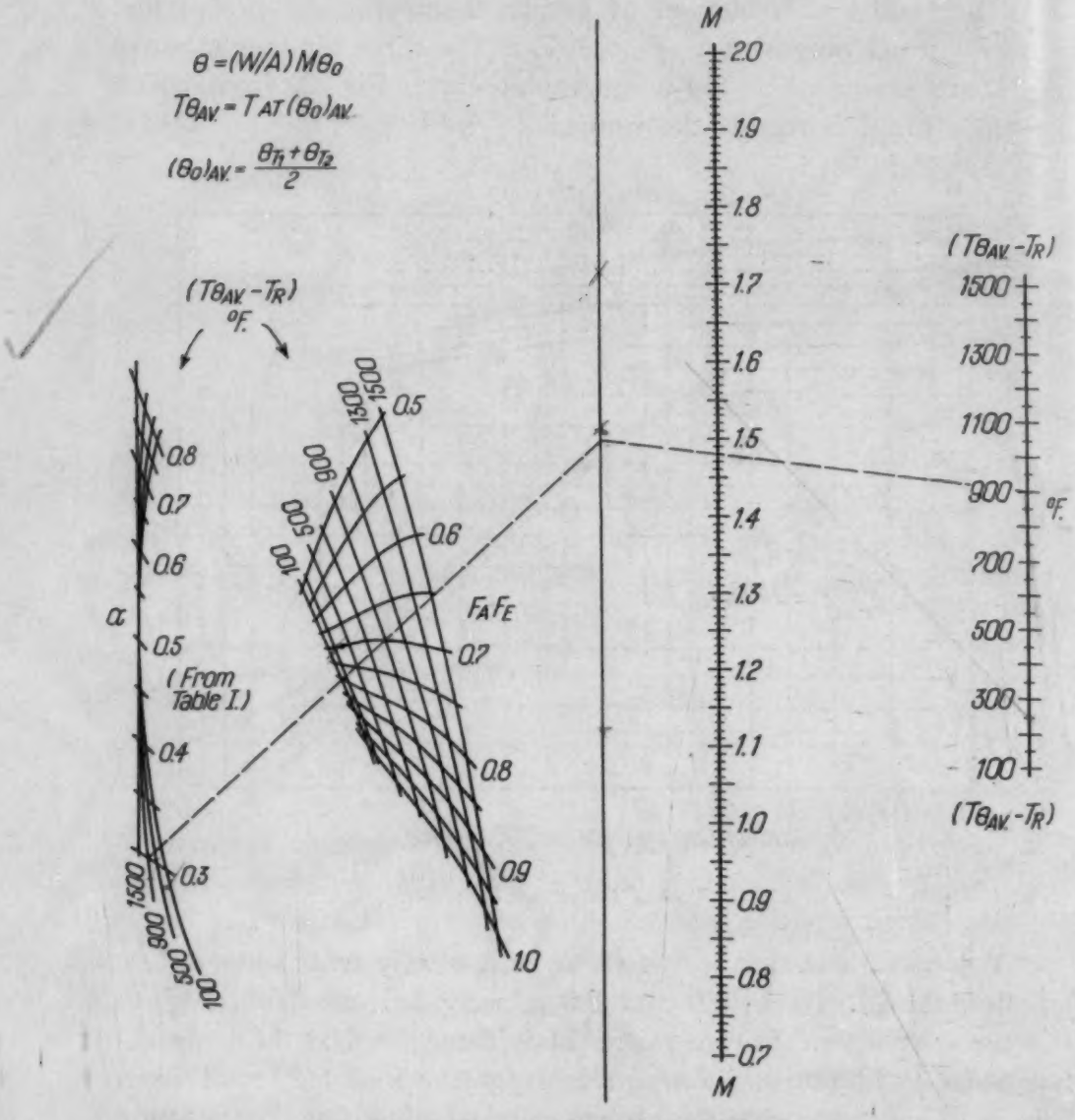

Fig. 2—Chart for Determining Multiplier.

The shapes tested included solid rounds, hexagons, squares, rectangles, and standard black pipe.

Fitting calculated curves to the experimental curves required trial calculations using assumed values of F_E and a. Until correct values of each were chosen, a good fit over the entire range was not obtainable. When correct values had been finally worked out, the test data and calculated curves for the mild steel bars frequently coincided to within experimental precision. Some of these calculated and experimental results are shown in Fig. 3.

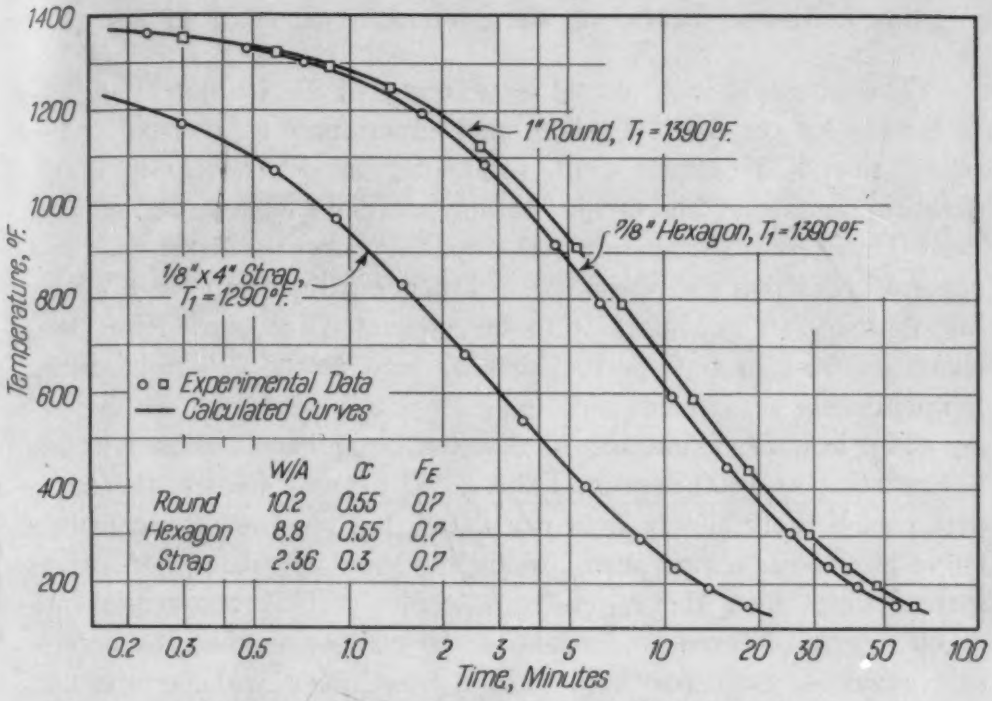

Fig. 3—Cooling Curves for Several Mild Steels.

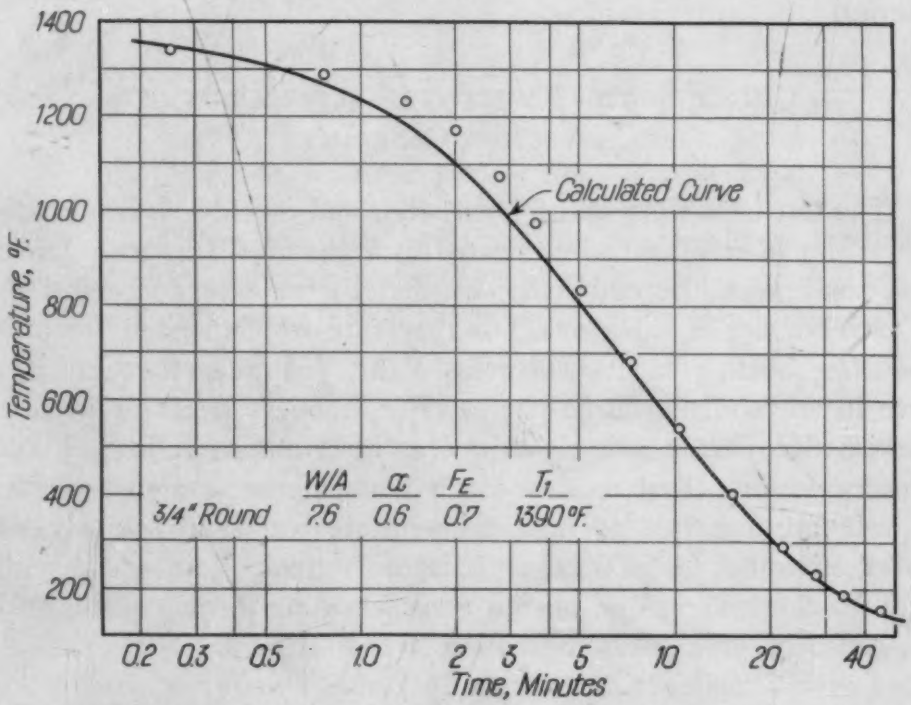

Fig. 4—Cooling Curve of a Eutectoid Steel.

Behavior of Carbon Steel

The solid ¾-inch round was reported to be eutectoid steel (0.8 per cent carbon). Carbon steel experiences a "thermal critical point" near 723 degrees Cent. (1333 degrees Fahr.), or at a temperature somewhat higher on heating, and somewhat lower on cooling. During the "transition", the cooling curve is distorted. It is general belief that the phenomenon is accompanied by energy effects, but Austin (1) considers it to be adequately accounted for by a sharp increase in the specific heat of iron at the "thermal critical temperature."

The best fit obtainable for the eutectoid bar is shown in Fig. 4. Starting at 1400 degrees Fahr. (760 degrees Cent.), the bar at first cooled more slowly than calculated, but rejoined the calculated curve at a lower temperature, giving the same calculated and experimental times over the range as a whole. This observation was checked several times, and leads to the conclusion that the correlation may be used for high carbon steel over wide temperature ranges. Over narrow ranges around 1200 degrees Fahr. (650 degrees Cent.) it will probably be found inaccurate for this type of material.

Choice of the Emissivity Factor and the Convection Constant

The test bars were all of plain steel, and quickly became coated with a film of millscale when heated in a gas-fired furnace. Under these conditions, the emissivity factor ($F_E = p$) approached 0.7 for each bar. The value of 0.7 is therefore recommended for plain steel after heating to 1000 degrees Fahr. (540 degrees Cent.) or above in an oxidizing atmosphere. For stainless steels or in cases in which the surface remains shiny (as in bright annealing), p may be much lower. Red oxides which have higher emissivities than millscale are unstable at high temperatures, and are quickly destroyed if heated to 1000 degrees Fahr.

Experimental values of the constant a in the correlation for the coefficient of natural convection

$$a = \frac{h_c}{(T - T_r)^{0.25}} \qquad (c)$$

are given in Table I. For the rounds, the corresponding value of k_c in equation (b)

$$h_c = \frac{k_c}{(D')^{0.25}} (T - T_r)^{0.25} \qquad (b)$$

is 0.56, which may be used for small solid rounds and pipes up to 1 inch diameter. McAdams (4) gives 0.42 for larger pipes in horizontal position, and lists correlations for other cases.

Radiation Angle Factor for a Row of Bars

In the hot mill of a steel plant, hot-rolled bars are racked in single rows for cooling. Radiation loss is reduced, since the angle

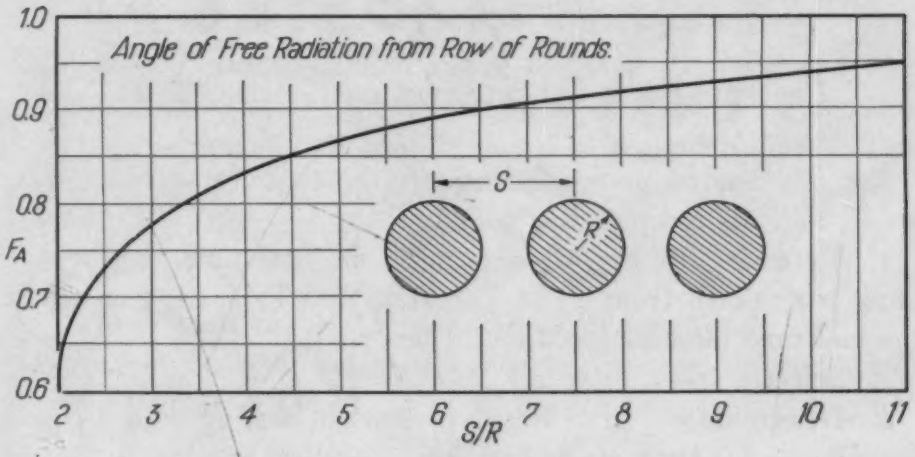

Fig. 5—Angle of Free Radiation from Row of Rounds.

factor F_A is then less than unity. Here, the angle of free radiation is desired, whereas commonly reported values of F_A are for *intercepted* radiation. The relation between the two is

$$F_{A\,(\text{free})} = 1 - F_{A\,(\text{intercepted})}$$

Fig. 5 gives the free radiant angle for a row of rounds of radius R, spaced at distance S between centers. Fig. 6 gives the free radiant angle for a row of squares or rectangles, in terms of their shape and spacing. Fig. 6 was developed from the data of Hottel (2) for long parallel rectangles.

Free radiant angles for squares and rounds similarly spaced are not greatly different unless laid quite close together. Free radiant angles for other shapes such as hexagons and twisted squares (reinforcing steel) fall *between* corresponding values from Figs. 5 and 6.

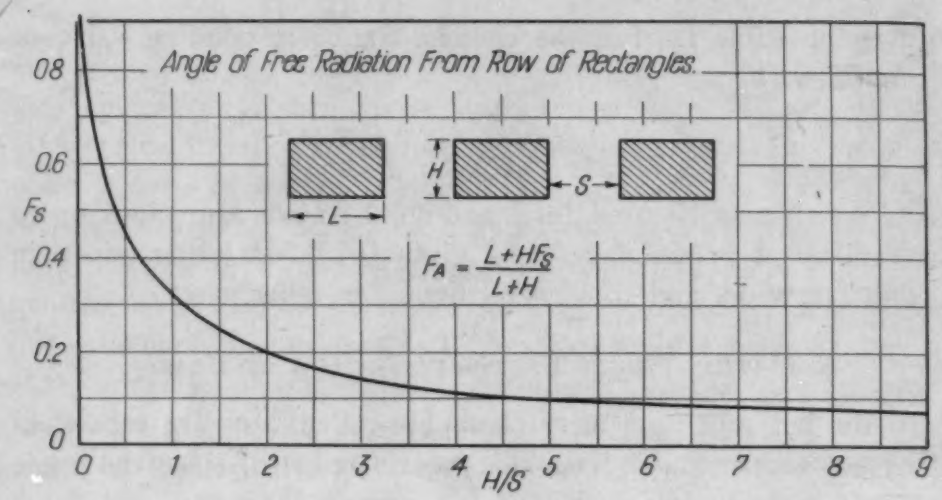

Fig. 6—Angle of Free Radiation from Row of Rectangles.

Procedure for Calculation of Cooling Time

For any bar of given dimensions, the time for cooling in air from T_1 to T_2 is computed as follows:

1. Referring to Fig. 1, determine Θ_o, the time required for the unit bar to cool from T_1 to T_2. Also find $T_{\theta av.}$, the temperature at the mid-time interval for the unit bar.

2. Select a from Table I.

3. Determine F_A from Fig. 5 or 6 when dealing with a row of bars. ($F_A = 1.0$ for a single bar.)

4. Estimate F_E. ($= 0.7$ for plain iron or carbon steel, if heated above 1000 degrees Fahr. recently.)

Table I

Values of Convection Constant a

	Diameter, or Smallest Thickness, Inches				
	⅛	½	¾	⅞	1
Rounds	...	0.7	0.6	....	0.55
Hexagons	...	0.65	...	0.55	....
Squares	...	0.6	...	....	....
Rectangles	...	0.4	(2 inches wide. Either flat or on edge.)		
	0.3	...	(4 inches wide. Either flat or on edge.)		

For rounds up to 1 inch diameter:

$$a = \frac{0.56}{(D')^{0.25}}$$

For rounds over 1 inch diameter:

$$a = \frac{0.42}{(D')^{0.25}}$$

For millscaled iron surfaces, $p = 0.7$. For other surfaces, see Ref. (3).

5. Determine M from Fig. 2, at $(T_{\theta av.} - T_R)$.

6. Calculate W/A as pounds per square foot surface area. (Density of mild steel = 7.8 = 485 pounds per cubic foot).

The desired time is then

$$\Theta = (W/A)\ M\ \Theta_o$$

Since a single temperature was used in obtaining M, the time so calculated may be slightly in error, although usually by less than 2 per cent. If greater accuracy is desired, M should be evaluated as follows: Divide Θ_o into two or more smaller equal intervals, and determine values of M at $(T_{\theta av.} - T_r)$ for each interval. These values for M are then averaged, and the average used as before.

Illustration

Annealed steel condenser tubes 1½ inch diameter and No. 10 B. W. G. wall are to be racked in a row at 1200 degrees Fahr., spaced on 6-inch centers, and allowed to cool to 300 degrees Fahr. The air temperature is 100 degrees Fahr. Calculate the time required.

Solution

From Fig. 1, $\Theta_o = 2.5 - 0.26 = 2.24$ minutes.

$\Theta_{av.} = (2.5 + 0.26)/2 = 1.38$ min.; $T_{\theta av.} = 480$ degrees Fahr.

From Eq. 2, Table I,

$$a = \frac{0.42}{(D')^{0.25}} = \frac{0.42}{(1.5)^{0.25}} = 0.38$$

From Fig. 5, S/R = 6/1.5 = 4; $F_A = 0.83$.

Take $F_E = 0.7$; then $F_A F_E = 0.58$

From Fig. 2, $(T_{\theta av.} - T_r) = (480 - 100) = 380$; M = 1.51

From a table of condenser tube data,

W = 2.12 lb./linear ft.

A = 0.3925 sq.ft./linear ft.

W/A = 5.4

$\Theta = (5.4)\ (1.51)\ (2.24) = 18.3$ minutes. *Ans.*

(An accurate evaluation of M gave 18.4 minutes in this case.)

Nomenclature

A	Outside surface area of bar or tube, *sq. ft./ft.*
C	Specific heat of iron.
D′	Outside diameter of round bar or tube, inches.

over

F_A Angle factor for free radiation. (1.0 for single bar. For single rows, see Figs. 5 and 6.) Dimensionless.

F_E Radiation emissivity factor (= p, black body coefficient.) p = 0.7 for plain iron and carbon steel, atmospheric oxidized at 1000 degrees Fahr. or above. For other surfaces, see ref. 3.

h_c Convection heat loss coefficient, *B.T.U./(sq.ft.)(hr.)(degrees Fahr.).*

h_r Radiation heat loss coefficient, *B.T.U./(sq.ft.)(hr.)(degrees Fahr.).*

K Radiation constant = $10^8/0.173\ F_A F_E$.

k_c Constant for rounds in convection correlation. See Eq. (b) and Table I.

M Multiplier in Eq. (i), obtained from Fig. 2.

Q Rate of heat loss, *B.T.U. per hour.*

T Temperature of bar at any moment, *°R. or °F.*

T_r Air temperature, *°R. or °F.*

$T\ \theta_{av}$ Temperature at mid-time interval of unit bar, *°R. or °F.*

W Weight of bar, *pounds per foot.*

Greek Letters

α Constant in convection correlation depending upon size and shape of bar. See Table I.

θ Time required for cooling from T_1 to T_2, minutes.

θ_o Time required for unit bar to cool from T_1 to T_2, minutes.

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4. Walker, Lewis, McAdams, and Gilliland, *Principles of Chemical Engineering*, eq. 23a, p. 133, 3rd Ed., 1937.
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6. *Ibid*, Eq. 37, p. 160.

A METHOD OF DEFINING FAILURE IN MEMBERS SUBJECTED TO COMBINED STRESSES

By Joseph Marin

Abstract

For ductile metals and alloys which do not have a definite yield point a measure of the strength corresponding to this point is usually obtained by the "yield point strength" as defined using the offset method. This is a stress which corresponds to a permanent deformation of a prescribed amount. The procedure using this method has been applied to the tension test only. If the specimen is subjected to bending, torsion or a combined state of stress it would be desirable to define the yield strength in such a way that it can be correlated to the yield strength in tension. This paper attempts to make this correlation. For this purpose graphs are presented giving offset strain values to be used in torsion or combined stresses—such strains corresponding to the offset strain used in the usual tension test.

Introduction

In recent years more attention has been applied to determining the state of stress in structural and machine members. For this purpose the strain rosette method has received considerable attention (1), (2), (3), (4), (5).[1] This method is used in the testing of structural members in which a combined state of stress occurs and in which the state of stress is determined from strain readings taken in several directions at a point (1). From such readings the principal strains and stresses can be determined. It is of importance not only to evaluate the principal stresses for a given load on a structural member but also to define the point of failure. For ductile metals which have a lower and upper yield point, the point of failure is usually defined by the lower yield point (6), (7). On the other hand, for ductile metals which do not have a definite yield point, the determination of the point of failure in the case of a combined state

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

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of stress presents a problem. This paper develops a method for defining the beginning of failure in the case of combined stresses, and is based on the assumption that failure in the case of combined stresses occurs when the maximum principal strain is equal to the strain value defining failure in the case of simple tension. It is first convenient to define failure in simple tension.

Failure in Simple Tension

The stress-strain relation for many ductile metals in simple tension is of the type shown in Fig. 1, such that a yield point is not

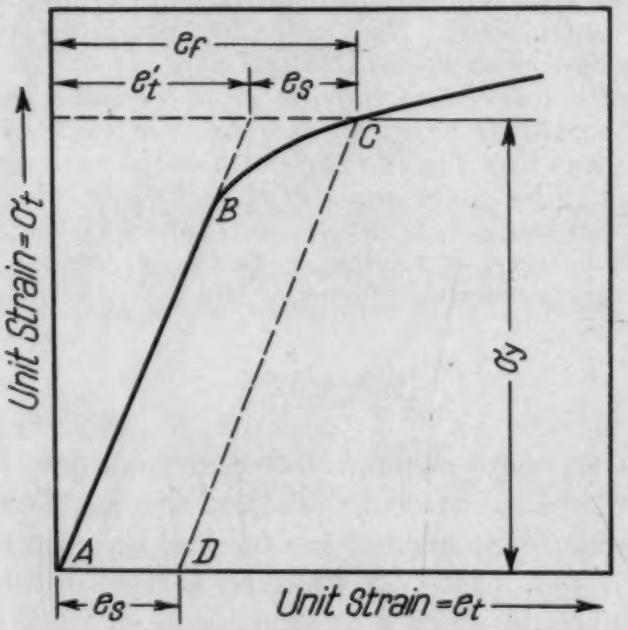

Fig. 1—Stress-Strain Relation in Simple Tension.

definitely defined. In the case of simple tension, failure is usually stated for such materials by specifying a permanent set AD = e_s and the yield strength or failure stress is then defined by the point C obtained by drawing DC parallel to AB (8).

Failure in Structural and Machine Members Subjected to Combined Stresses

In the general case of two-dimensional stress there are three stress components σ_x, σ_y, τ_{xy} as shown in Fig. 2. The corresponding strain components are e_x, e_y and e_{xy}. Then for an element abcd the strain in the direction θ is:

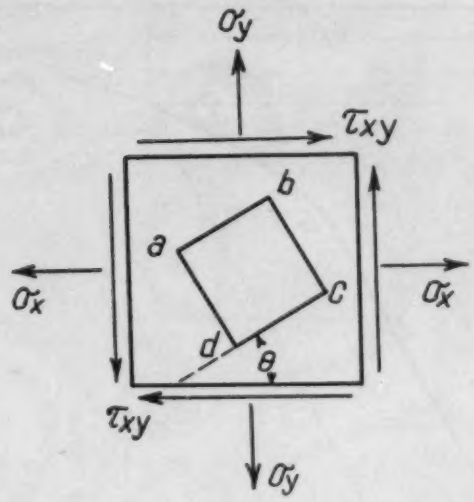

Fig. 2—Stress Components for Combined Stress.

$$e = e_x \cos^2\theta + e_y \sin^2\theta + e_{xy} \sin\theta \cdot \cos\theta \quad \ldots\ldots\ldots\ldots (a)$$

The maximum principal strain is obtained by placing $\frac{\partial e}{\theta} = 0$

From equation (a) this maximum strain occurs for a value of θ which is defined by

$$\tan 2\theta = \frac{e_{xy}}{e_x - e_y} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (b)$$

Placing the value of θ from (b) in (a), the maximum principal strain is:

$$e_1 = \tfrac{1}{2} [e_x + e_y + \sqrt{(e_x - e_y)^2 + e_{xy}^2}] \quad \ldots\ldots\ldots\ldots (c)$$

The maximum principal stress corresponding to the strain e_1 can now be obtained in terms of the stress components. Its value is

$$\sigma_1 = \frac{\sigma_x + \sigma_y}{2} + \sqrt{\left(\frac{\sigma_x - \sigma_y}{2}\right)^2 + \tau_{xy}^2} \quad \ldots\ldots\ldots\ldots\ldots (d)$$

Consider now a test of a structural or machine member in which readings of strains are taken for various increments of load. For a given load the value of σ_1 can be calculated from equation (d) and the corresponding value of the maximum principal strain determined from equation (c). They can also be evaluated graphically by using the Land circle as utilized in the strain rosette method. A plot relating σ_1 and e_1 can then be constructed as shown in Fig. 3. Failure will now be defined by the point C in Fig. 3, such that the unit strain e_f in the case of a combined state of stress is equal to the strain e_f in

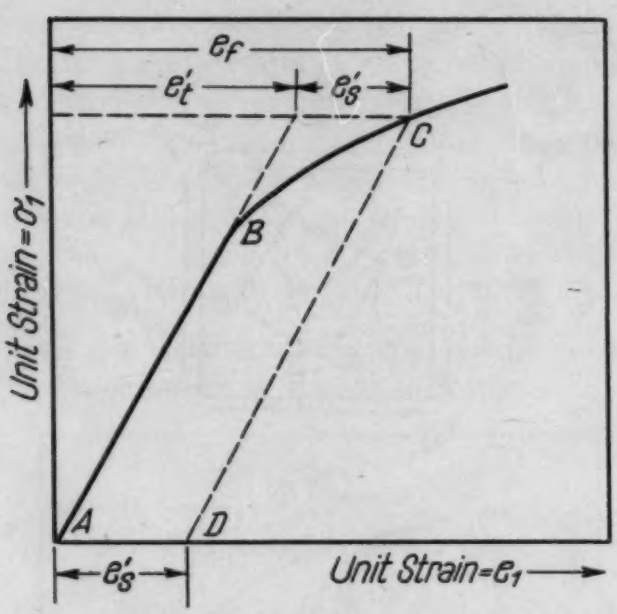

Fig. 3—Stress-Strain Relation for Principal Stresses.

the case of simple tension at failure (Fig. 1). That is, failure occurs for

$$e_t^1 + e_s = e_1^1 + e_s^1 \quad \ldots\ldots (e)$$

To fix the position of point C in Fig. 3 it is necessary to determine AD $= e_s^1$. From equation (e),

$$e_s^1 = (e_t^1 + e_s) - e_1^1 \quad \ldots\ldots (f)$$

If σ_{yp} = the stress at failure in simple tension, then the strain intercept e_t^1 is:

$$e_t^1 = \frac{\sigma_{yp}}{E} \quad \ldots\ldots (g)$$

A common value used for e_s is 0.002 inch per inch. Then from equation (c) the principal strain e_1^1 becomes

$$e_1^1 = \tfrac{1}{2}\left[e_x^1 + e_y^1 + \sqrt{(e_x^1 - e_y^1)^2 + e_{xy}^2}\right] \quad \ldots\ldots (h)$$

Placing values of e_t^1 and e_1^1 from (g) and (h) in (f), the permanent set value AD for the combined state of stress is:

$$e_s^1 = \left(\frac{\sigma_{yp}}{E} + e_s\right) - \tfrac{1}{2}\left[e_x^1 + e_y^1 + \sqrt{(e_x^1 - e_y^1)^2 + (e_{xy}^1)^2}\right] \quad \ldots\ldots (1)$$

The determination of the value of e_s^1 from equation (1) must necessarily be one of successive approximations since the values of the strain components e_x^1, e_y^1 and e_{xy}^1 depend upon the value of the loads

at failure. This does not, however, involve much work since two or three trials are sufficient.

To give an indication of the relative values of the permanent set e_s^1 compared to the values in simple tension, consider the principal stresses σ_1 and σ_2 shown in Fig. 4. In structural members in which

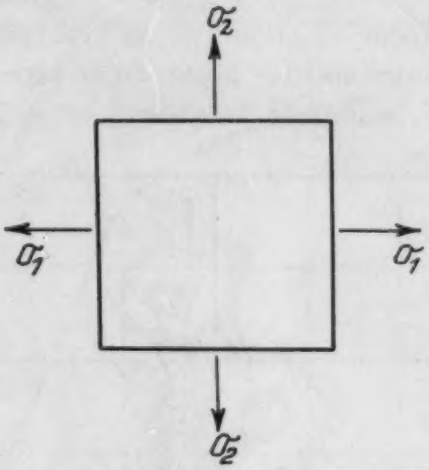

Fig. 4—Element Subjected to Principal Stresses.

the strain rosette method is used, the values of the principal stresses σ_1, σ_2 and the principal strains e_1 and e_2 can be determined. Then from equation (1), noting that $e_{xy}^1 = 0$, $e_x^1 = e_1^1$, $e_y^1 = e_2^1$, the strain e_s^1 is:

$$e_s^1 = \left(\frac{\sigma_{yp}}{E} + e_s\right) - e_1^1 \quad \text{.....(i)}$$

and since

$$e_1^1 = \frac{\sigma_1^1}{E} - \nu \frac{\sigma_2^1}{E} \quad \text{.....(j)}$$

Then

$$e_s^1 = \left(\frac{\sigma_{yp}}{E} + e_s\right) - (\sigma_1^1 - \nu\,\sigma_2^1)\,\frac{1}{E} \quad \text{.....(k)}$$

or

$$e_s^1 = \left(\frac{\sigma_{yp}}{E} + e_s\right) - \frac{\sigma_1^1}{E}\left[1 - \nu \frac{\sigma_2^1}{\sigma_1^1}\right] \quad \text{.....(l)}$$

If it is now assumed that failure is defined by the distortion energy theory then

$$(\sigma_1^1)^2 - \sigma_1^1\,\sigma_2^1 + (\sigma_2^1)^2 = \sigma_{yp}^2 \quad \text{.....(m)}$$

or

$$\sigma_1^1 = \frac{\sigma_{yp}}{\sqrt{1 - R + R^2}} \quad \text{.....(n)}$$

where

$$R = \sigma_2^1/\sigma_1^1$$

Placing the value of σ_1^1 from (n) in (1):

$$e_s^1 = \frac{\sigma_{yp}}{E}\left[1 - \frac{1 - vR}{\sqrt{1 - R + R^2}}\right] + e_s \quad \ldots\ldots\ldots\ldots (2)$$

It is now possible from equation (2) to evaluate the permanent set e_s^1 for a given material and for a particular ratio R of the principal stresses. In Fig. 5, values of permanent set e_s^1 are plotted versus

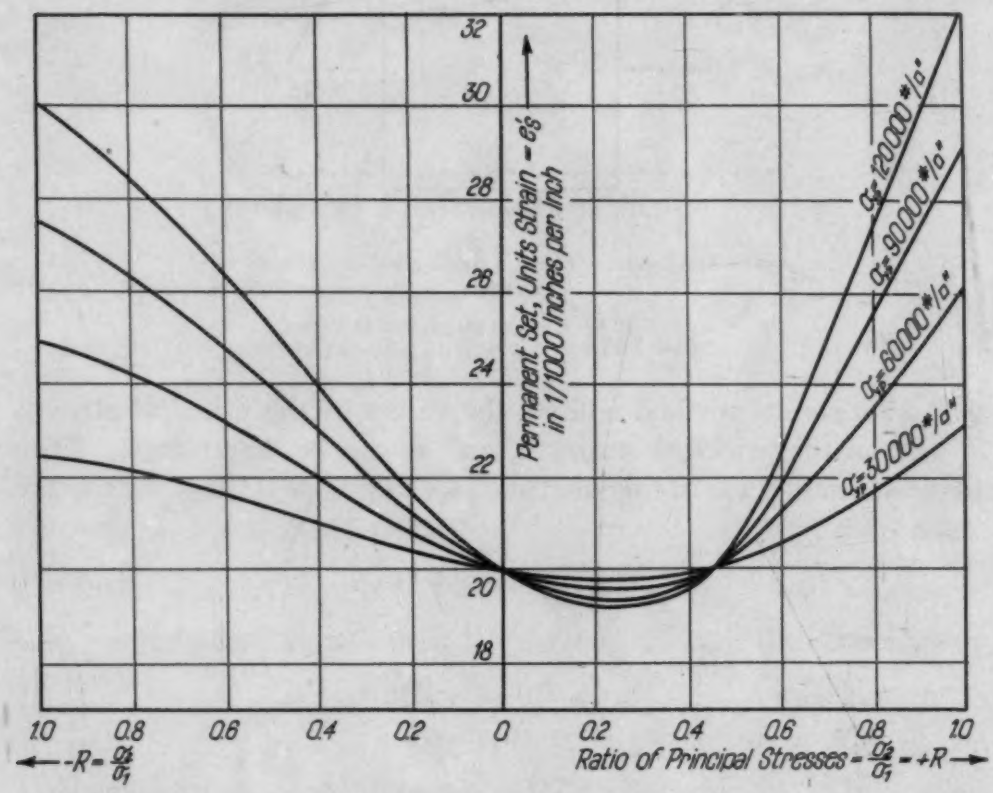

Fig. 5—Offset Strain Values for Defining Yielding in the Case of Combined Stresses.

the stress ratio R for values of $E = 30 \times 10^6$ pounds per square inch, $v = 0.3$, $e_s = 0.002$ inch per inch, and for various values of σ_{yp}—the stress at failure in simple tension. These graphs would be applicable to various kinds of steel and other ductile metals. It is of significance to note that the permanent set value for most ratios of principal stresses can be increased over the value used for simple tension. For $\sigma_{yp} = 120{,}000$ pounds per square inch, this increase is as much as 60 per cent.

Special Case of Pure Torsion

In a torsion test, a plot is made between the angle of twist and the twisting moment. If the material is such that a lower and upper yield point is not present as in Fig. 6, it is desirable to have a method

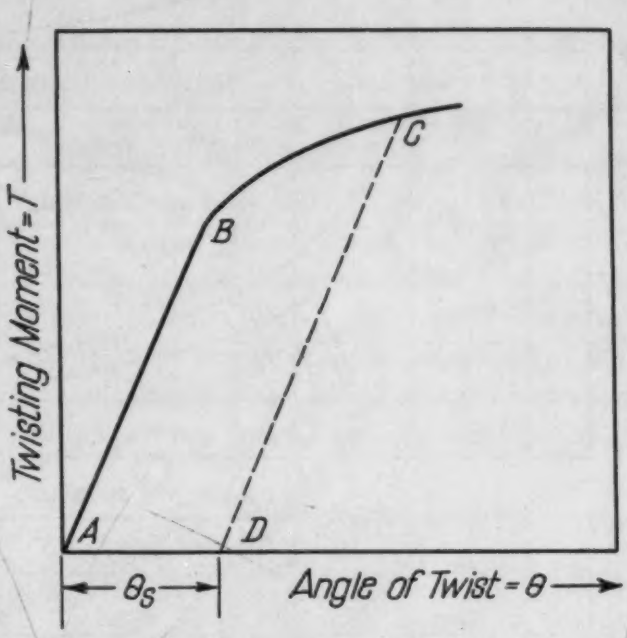

Fig. 6—Torque-Twist Diagram.

of defining failure so that the strength in torsion can be correlated with the strength in simple tension. In other words, it is consistent to define failure in torsion by the point C in Fig. 6, where the permanent set angle θ_s is equivalent to the permanent set e_s in simple tension. To evaluate θ_s consider equation (2). For the case of pure torsion,

$$\sigma_1 = + \tau_{xy} \text{ and } \sigma_2 = - \tau_{xy} \quad \text{.....(o)}$$

Then

$$\sigma_2/\sigma_1 = R = -1 \quad \text{.....(p)}$$

Placing a value of R = — 1 in equation (2),

$$e_s^1 = \frac{\sigma_{yp}}{E}\left[1 - \left(\frac{1+v}{\sqrt{3}}\right)\right] + e_s \quad \text{.....(q)}$$

For the case of torsion using equation (c), since

$$e_1 = e_s^1,\ e_x = e_y = 0,\ e_{xy} = (e_{xy}^1)_s$$

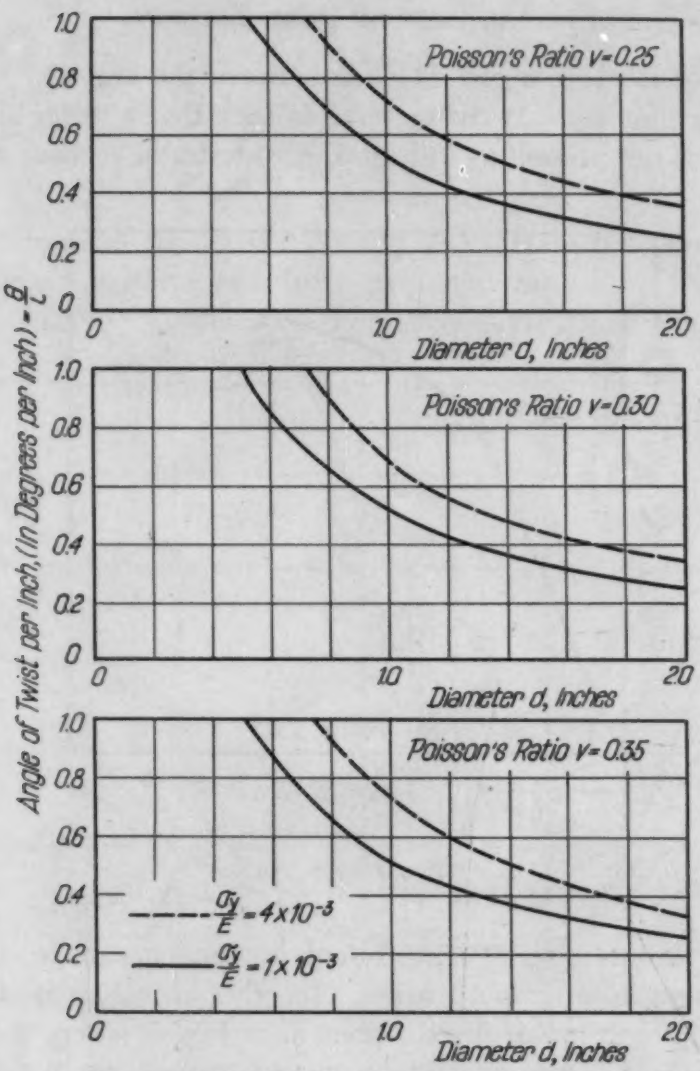

Fig. 7—Offset Angles of Twist for Defining Yielding in Torsion.

then

$$e_s^1 = \frac{(e_{xy}^1)_s}{2} \quad \text{(r)}$$

If θ_s = the angle of twist, d = diameter of specimen, L = gage length, then

$$(e_{xy}^1)_s = \frac{d\,\theta_s}{2L} \quad \text{(s)}$$

From equations (q) (r) and (s),

$$\left(\frac{\theta_s}{L}\right) = \frac{4}{d}\left[\frac{\sigma_{yp}}{E}\left\{1 - \left(\frac{1+\nu}{\sqrt{3}}\right)\right\} + e_s\right] \quad (3)$$

For a given material the permanent set angle θ_s is defined by equation

(3). Fig. 7 gives an indication of the variation in the value of θ_s/L for various values of the diameter of specimen d and different values of Poisson's ratio.

Concluding Remarks

A method has been presented in the above discussion for defining failure in testing of structural members subjected to combined stresses. The method is of use in cases where the material considered has no definite yield point. The procedure developed gives a consistent relation between failure in simple tension and failure in members subjected to combined stresses. This is of particular importance since design is based usually on tests of materials subjected to simple tension. A method of defining failure in the case of torsion, consistent with simple tension, was also discussed. This method affords a means of correlating strength in torsion and tension for materials which do not have a definite yield point.

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NUCLEATION AND GROWTH RATES OF PEARLITE

By J. E. Dorn, E. P. De Garmo and A. E. Flanigan

Abstract

Extension of the Johnson-Mehl theory of the formation of pearlite to yield nodules observed-time relationships for small fractions transformed, permits a simple and rapid determination of the nucleation and growth constants for pearlite. Investigations on a single steel indicate that the nucleation and growth constants are independent of time. Pearlite transformation for the steel which was examined is not isokinetic. Data on the variation of G and N with temperature are presented.

Introduction

DURING the last few years several theories on nucleation and growth of pearlite have been suggested. Göler and Sachs (1)[1] introduced the analytical approach to the subject and derived a fraction transformed-time curve for the special case of general volume nucleation and spherical growth of nodules. The Göler-Sachs theory, however, did not account for impingement of nodules during growth and austenitic grain size. A single fraction transformed-time curve was developed which did not agree with the experimental facts for large percentages transformed. Mehl (2) and subsequently Johnson and Mehl (3) developed a more rational approach to the problem of the formation of pearlite by introducing into the analysis certain observed facts on the growth of pearlite nodules. The following assumptions were made:

a. Austenite grains may be considered perfect spheres of constant radius. Although this assumption is not absolutely true it is sufficiently exact to be a useful simplification of the observed facts.
b. Pearlite nucleates at the austenite grain boundaries. The occasional nodule nucleated in the grain volume due to the

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

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presence of an inclusion or other imperfection is not considered in the Johnson-Mehl theory.

c. The number of nuclei formed per second is proportional to the untransformed surface. The constant of proportionality which is called the nucleation constant is assumed to be independent of time.

d. Pearlite nodules grow with a constant radial growth rate.

e. Pearlite nodules do not grow across the austenite grain boundaries. This assumption agrees with microscopic examination of pearlite growth.

f. When pearlite nodules impinge growth ceases.

On the basis of these assumptions it was shown that the fraction transformed may be expressed as a function of two dimensionless moduli, namely:

$$V \equiv V\ (\lambda, z) \qquad [1]$$

where $$\lambda = \frac{\pi a^3 N}{3G} \qquad [2]$$

and $$z = \frac{Gt}{a} \qquad [3]$$

$t =$ time
$a =$ radius of austenite grain
$N =$ nucleation constant
$G =$ linear growth constant

Thus, for each value of the shape factor λ, a slightly altered fraction transformed $\frac{Gt}{a}$ curve results as shown in Fig. 1 (4). A semilogarithmic plot of the experimentally determined Fraction Transformed-Time relationship may be fitted to one of the "Master Curves" of the theory to evaluate N and G, provided a is known. The shapes of the master curves do not change significantly even for relatively large changes in λ. Consequently the values of N and G evaluated from the master curves of Fig. 1 are subject to serious error even when the theory approximates the experimental facts.

It was suggested by Johnson and Mehl that their theory may require slight modification if N and G are not constants. Scheil and Lange-Weise (5) and subsequently Mehl (2) have shown that determinations of the radius of the maximum pearlite nodule as a function of time indicate that G is a constant. Data on N is very meager and unsatisfactory. The results of Scheil and Lange-Weise appear to indicate that N increases with time, but the statistical method employed to analyze their data may have been at fault.

Avrami (6) recently suggested that nuclei of a new phase may not form spontaneously but that they originate from a finite number of germ nuclei. As transformation proceeds the germ nuclei disappear due to the fact that they mature and grow into nodules or due to the fact that the growing nodules absorb the germ nuclei as they spread over the old phase. Fairly good proof of this mechanism

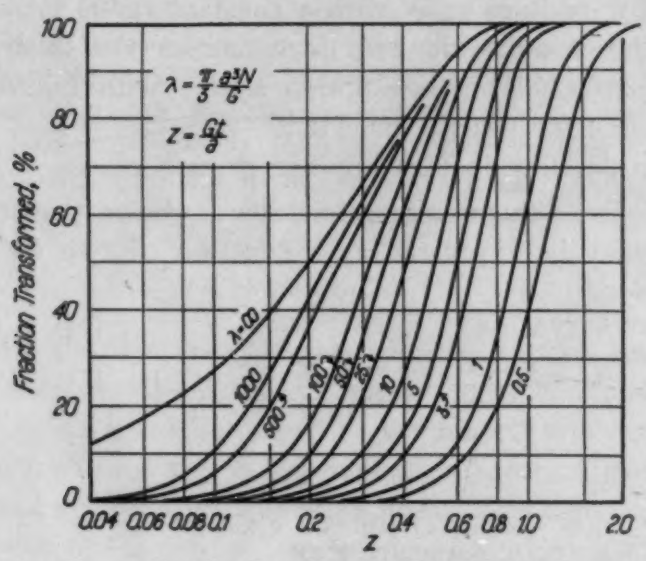

Fig. 1—Fraction Transformed—Time Master Curve.

for solidification exists. Avrami, however, assumes that this mechanism is also valid for the formation of decomposition products of austenite. If this be true N in the Johnson-Mehl theory should diminish with time unless the number of germ nuclei present is infinitely great. The mathematical approach of Avrami has certain desirable features of simplicity over the Johnson-Mehl theory. On the other hand Avrami has neglected the effect of grain size on the rate of transformation. Except for the points mentioned the two theories are reasonably similar and it is a simple matter to combine the virtues of both methods of approach.

The present investigation represents an attempt to weigh Avrami's assumption of germ nuclei and to study the process of nucleation and growth of pearlite in a eutectoid steel.

Theory

Due to the fact that the master curves of Fig. 1 are insensitive to changes in λ and hence changes in N, a check between experimental

data and the master curve cannot be considered proof that the assumptions of constancy of G and N are valid. Investigations on the number of nuclei as a function of time should yield more accurate data for detecting variations in N as pearlite forms. In consequence of the statistical nature of the problem, however, the approach cannot be direct, and therefore a brief introduction to the theory of the present measurements will be given.

Let us assume tentatively that the Johnson-Mehl concept of spontaneous nucleation of pearlite at random over the entire grain boundary of austenite is valid. In terms of Avrami's theory this means that the number of germ nuclei initially present on the austenite grain boundary is very large with respect to the number of nuclei that actually mature. It will be shown later that this assumption leads to expressions that are in good agreement with the experimental facts for the single steel that was examined. For this steel, therefore, Avrami's assumption of germ nuclei is an unnecessary complicating factor.

The rate of formation of pearlite nodules on the surface of a representative austenite grain is:

$$\frac{dn}{dT} = 4\pi a^2 N\{1 - S(T)\} \qquad [4]$$

where $S(T)$ equals the fraction of the surface which was transformed at time T. On the basis of Avrami's formulation, but Johnson and Mehl's assumptions:

$$1 - S(T) = e^{-S(T)_{ex}} \qquad [5]$$

where $S(T)_{ex}$ is the extended transformed surface per unit original surface and equals:

$$S(T)_{ex} = \frac{\pi}{3} NG^3T^3 = \lambda Z^3 \qquad [6]$$

$$\text{where} \quad Z = \frac{GT}{a} \qquad [7]$$

Accordingly the number of nuclei formed on a single austenite grain is:

$$dn = 12\lambda e^{-\lambda Z^3} dZ \qquad [8]$$

or if $\lambda Z^3 < 1$

$$dn = 12\lambda \left\{1 - \lambda Z^3 + \frac{(\lambda Z^3)^2}{2!} - \ldots.\right\} dZ \qquad [9]$$

Let us now consider the probability of a plane of polish cutting a

nodule of pearlite of radius r in an austenite grain of radius a. As shown in Fig. 2 not all planes cutting the austenite grain cut the nodule. A random plane of polish at an angle Θ will on the average cut the nodule over region X as shown by the broken lines. Since

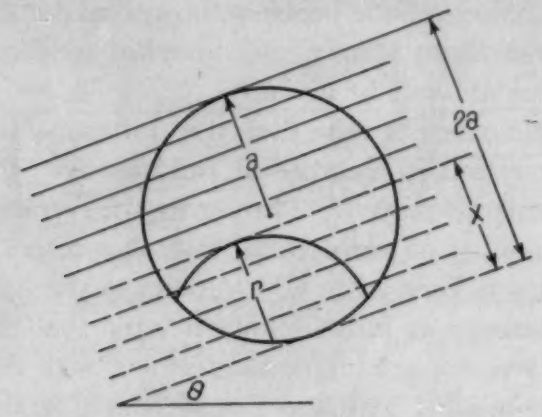

Fig. 2—Probability of Seeing a Nodule.

this same plane of polish cuts a single austenite grain over region 2a, the probability of cutting the nodule is $\frac{X}{2a}$ for the single orientation selected. Averaging this over all possible orientations yields (4):

$$P = \frac{1}{\pi}\left\{ 2 \arcsin\frac{r}{2a} + \frac{r}{a}\arccos\frac{r}{2a}\right\} \quad [10]$$

Thus it is noted from Fig. 2 and equation 10 that as the radius of a pearlite nodule increases, a greater number of nodules will be observed per grain cut even when no new nodules have nucleated.

Equations 9 and 10 may now be combined to yield the number of nodules observed on a plane of polish for the limiting case where impingement is minor. The resulting equation is quite accurate up to 25 per cent volume transformed. Beyond this point it is almost impossible to count nuclei on a plane of polish and hence no attempt was made to extend the calculation beyond the useful range. In the range considered:

$$\frac{r}{a} = \frac{G(t-T)}{a} = z - Z \quad [11]$$

and

$$E = \int P\, dn = \frac{12\lambda}{\pi}\int_0^{Z=z}\left\{2 \arcsin\left(\frac{z-Z}{2}\right) + (z-Z)\arccos\left(\frac{z-Z}{2}\right)\right\} dZ \quad [12]$$

where E is the number of nuclei observed per austenite grain cut. This reduces to:

$$E = \frac{24\lambda}{\pi}\left\{ z \arcsin\frac{z}{2} + \left(\frac{z^2}{4} - \frac{1}{2}\right)\arccos\frac{z}{2} + \left(2 - \frac{z}{4}\right)\sqrt{1 - \frac{z^2}{4}} + \frac{\pi}{2} - 2\right\} \quad [13]$$

Fig. 3 is a semilogarithmic master chart that correlates the average number of nodules observed on a plane of polish cutting a single

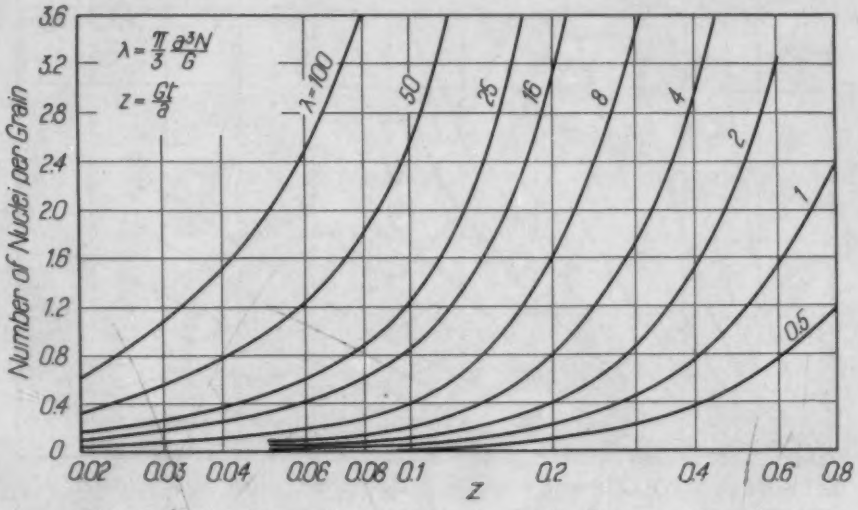

Fig. 3—Nuclei Observed per Austenite Grain Cut as a Function of λ and Z.

austenite grain. It is interesting to note that E as well as V is a function of λ and z. E, however, is much more sensitive to changes in λ than V. The master chart for nucleation of Fig. 3 may be used in a similar manner to the master chart for fraction transformed of Fig. 1. Consequently it suffices to establish N and G when a is known, by matching the experimental graph of the number of nodules observed per grain versus time to one of the theoretical curves.

The two relationships:

$$\begin{cases} V \equiv V(\lambda, z) \\ E \equiv E(\lambda, z) \end{cases} \quad [14]$$

may be solved simultaneously for the two quantities λ and z. Therefore

$$\begin{cases} \lambda = (V, E) \\ z = z(V, E) \end{cases} \quad [15]$$

Consequently it is possible to determine λ and z from a single photomicrograph by determining the fraction transformed and the number of nodules cut per austenite grain cut by the plane of polish. If the above theory is correct, a single photomicrograph will permit the calculation of the fraction transformed versus time curve and the number of nuclei versus time curve.

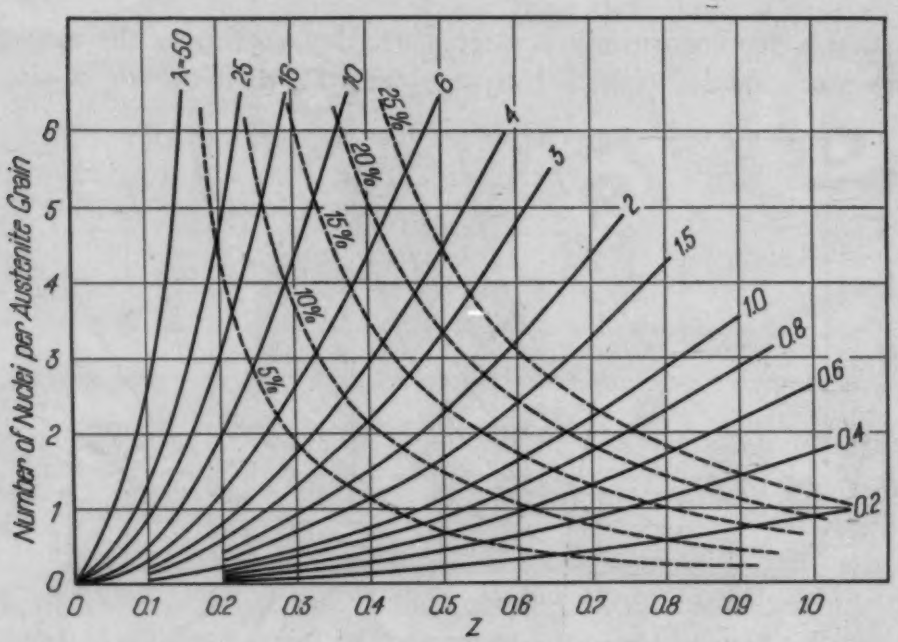

Fig. 4—Number of Nuclei Observed—Fraction Transformed Master Chart.

The simultaneous solution of equations 14 is most conveniently represented by the master chart of Fig. 4. If, for example, a single photomicrograph of pearlite nodules shows 10 per cent transformed and 1.0 nodule per austenite grain cut, start at the origin and go vertically on Fig. 4 to E = 1 and then horizontally up to the broken 10 per cent line. This point coincides with the solid line $\lambda = 0.60$ at $z = 0.62$. Therefore,

$$\lambda = \frac{\pi a^3 N}{3 G} = 0.60$$

and

$$z = \frac{Gt}{a} = 0.62$$

If the time at the transformation temperature and the austenite grain size are known G can be evaluated. N may be determined by:

$$N = \lambda\left(\frac{3G}{\pi a^3}\right) = \lambda z\left(\frac{3}{\pi a^3 t}\right) = 0.60 \times 0.62\left(\frac{3}{\pi a^3 t}\right) \qquad [16]$$

Since N depends upon both λ and z the error in N is somewhat greater than the error in G.

Although a single photomicrograph may be used to determine N and G for a given time t, it is also possible to evaluate a series of Ns and Gs from a series of photomicrographs of steel treated at the same transformation temperature for a series of times. If the above theory is correct the values of N should all be identical and the values of G should likewise be constant independent of time. If, however, Avrami's concept of germ nuclei is correct then the values of N should decrease with time. In this case the Ns represent some average values of N over the range of time employed. It will be shown that N and G for the steel investigated are practically independent of time over the ranges of times and temperatures investigated.

Experimental Technique

Segregation in hot-rolled eutectoid steels presented some experimental difficulties. A steel, having the composition: carbon 0.92 per cent, manganese 1.53 per cent, silicon 0.20 and molybdenum 0.26 per cent, was finally selected since it exhibited less variation in radial and longitudinal segregation than several other steels that were examined. In most respects this steel appeared to be adequate for the test; although the composition was slightly hypereutectoid, free proeutectoid cementite could not be detected in the transformed product; from the A_1 temperature to 1125 degrees Fahr. (610 degrees Cent.) pearlite was the only decomposition product; although an occasional volume nodule nucleated at an inclusion, by far the greater number of nodules nucleated on the boundaries of the austenite grains. Fig. 5 showing Bain's curve for 10 per cent transformed over a limited range of temperatures further characterizes the steel used.

Although there was little change in segregation over short lengths of the bar, radial segregation persisted after a normalizing treatment. Consequently all measurements were made at the same radius and orientation. Two lengths cut from bars of the same heat were used, but each length reacted slightly differently to isothermal treatment. For this reason the data from the two lengths are not entirely comparable.

The original 1-inch bars were turned down to ¾ inch and wafers 0.090 inch thick were cut from the bar. All wafers were given the same austenizing treatment by holding at 1600 degrees Fahr. (870 degrees Cent.) for 10 minutes before quenching in the isothermal lead bath. This treatment produced 153 austenite grains

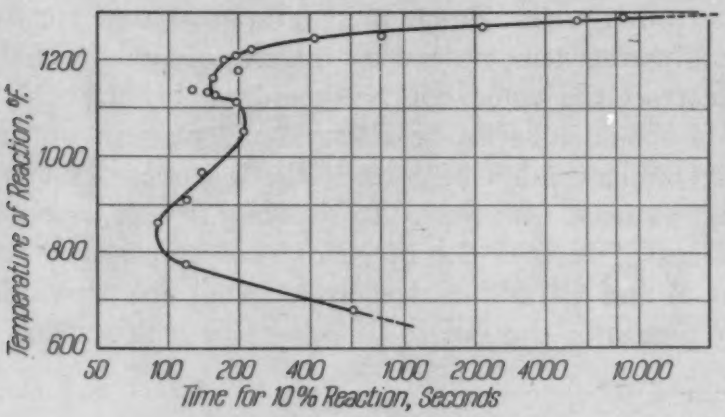

Fig. 5—Bain's Curve.

per square inch at 100 diameters, or a mean austenite grain radius of a = 0.00056 inch. Visual examination indicated a rather uniform grain size.

The isothermal treatment consisted of plunging the wafer from 1600 degrees Fahr. (870 degrees Cent.) into the constant temperature lead bath, holding, and then quenching in brine. Timing was accomplished by an electric stop watch actuated by a relay which made contact when the specimen struck the lead and broke contact when the specimen entered the brine. Decarburization occurred to a depth of not more than 0.005 inch and the surface was ground off 0.015 inch before polishing.

The number of nuclei was determined by direct microscopic count on electrolytically polished and etched wafers at 200 diameters. At this magnification the field was sufficiently large to make the count representative. The fraction transformed was determined in two ways. Comparison of images on the ground glass screen to prepared standard charts proved quite adequate when the number of the nodules approximated those on the standard charts. A second check using the fraction of a line intercepted by nodules was also satisfactory. In spite of the careful technique employed high accuracy on nuclei counts and percentage transformed was not attained

due to the difficulties normally encountered in measuring these quantities.

Discussion of Results

Inasmuch as a total of 225 individual tests were made, a detailed description of all of the results cannot be recorded here. The results, however, will be summarized by quoting a few typical examples.

The first study centered about the variation of G and N with time as revealed by an application of the master chart of Fig. 4. Five runs at a series of temperatures between 1130 and 1280 degrees Fahr. (610 and 695 degrees Cent.) were made. The data for short

Table I

$a = 56 \times 10^{-5}$
$T = 1155°$ F.

Time Sec.	E	V	z	λ	$G \times 10^{7}$	$N \times 10^{-8}$
61	0.41	1.0	0.35	0.7	32	12
75	0.59	1.2	0.32	1.1	23	14
88	0.73	2.5	0.35	1.3	22	16
105	0.90	6.5	0.48	0.9	25	12
110	1.14	7.0	0.46	1.2	23	15
119	1.58	12.0	0.53	1.3	25	17.5
		Mean value		1.1	25	14.5

times on the run at 1155 degrees Fahr. (625 degrees Cent.), a representative result, are shown in Table I. The three quantities λ, G, and N are independent of time as far as can be deduced from these results. Similar runs at higher temperature yielded the same general conclusions except that the spread of individual test values of G and N about the mean were greater than for the lower temperatures. This may be due to the fact that these quantities are more sensitive to slight changes in temperature at the higher temperatures. One test series at 1180 degrees Fahr. (640 degrees Cent.) indicated that N increased slightly with time whereas G in the same run decreased slightly with time. This anomalous result was charged to experimental error since runs about 20 degrees Fahr. on either side of the anomalous test series did not show this peculiarity. Consequently it was concluded that for the steel tested the nucleation and growth constants of pearlite are independent of time for the first half of the total reaction period (25 per cent transformed).

It is quite possible that the decrease in N postulated by Avrami occurs during the second half of the reaction period. This point was

checked by calculating the total fraction transformed-time curves from data obtained during the first half of the reaction period and comparing these curves with the experimentally determined data. Consider the run at T = 1155 degrees Fahr. (625 degrees Cent.) where $\lambda = 1.1$, and $\frac{G}{a} = 0.045 \frac{1}{\text{sec.}}$. The theoretical reaction curve for these average data is shown by the solid curve of Fig. 6. The broken curve represents the experimentally determined data. The

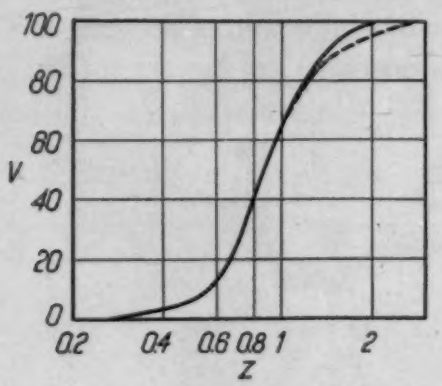

Fig. 6—Theoretical and Experimental Curves for Fraction Transformed.

two curves agree very well up to about 65 per cent transformed. For higher fractions transformed the theoretical curve is above the experimental curve. Similar results were obtained for all of the tests which were run.

For the steel employed it is possible to predict reaction curves up to about 65 per cent transformed from nucleation data at 0 to 25 per cent transformed. The theoretical curves indicate that the reaction terminates after a longer period of time than was predicted. Although these observations can be accounted for on the basis of Avrami's theory of germ nuclei, the evidence is not conclusive. Mehl (2) has shown that the same results accrue due to variation of austenitic grain size. Furthermore the nuclei that form near the end of the reaction contribute very little to the fraction of the volume transformed. Consequently it is believed that the assumption that N and G are constants is in fair agreement with the experimental results on the steel tested as shown by the fair agreement between theoretical and experimental curves such as Fig. 6.

Inasmuch as very little accurate or conclusive data on the nuclea-

tion constant N and the growth constant G as functions of temperature are available at present, a determination of these quantities was attempted. Application of the master charts of Fig. 4 permitted a rapid and fairly accurate determination of λ, G, and N. A small section of the original bar was used in the manner previously described in order to reduce the effect of longitudinal segregation on this determination. Two to four specimens were treated simultaneously and the points on the graphs represent average values of these determinations. For each specimen E and V were determined and λ, G, and N were evaluated by means of the master chart of Fig. 4.

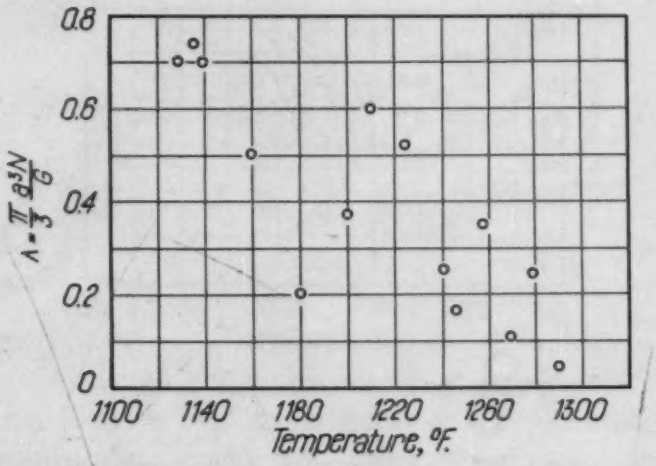

Fig. 7—The Shape Factor, λ, as a Function of Temperature.

Fig. 7 represents the data on λ. Some of the scattering of the experimental points is undoubtedly due to segregation. On the other hand the fraction of volume transformed is so insensitive to changes in λ that high accuracy in the measurement of this quantity is not easily attained. In spite of the scattered points there is an unmistakable trend in the data, indicating that λ decreases about one order of magnitude for an increase of 200 degrees Fahr. in this example. Furthermore, $\lambda = \frac{\pi a^3 N}{3 G}$ approaches zero as the A_1 temperature is reached.

It was suggested by Avrami that the rate of pearlite formation is isokinetic. On the basis of the Johnson-Mehl theory this means $\lambda = \frac{\pi a^3 N}{3 G}$ = constant for a constant austenitic grain size over the

entire pearlite temperature range. The present observations are in disagreement with Avrami's statement. If nucleation occurs on the grain boundary and growth takes place within the austenite grain, the assumption that N/G is a constant may no longer be legitimate because of the differences in the changes of activity of these dissimilar regions with temperature. On the other hand, the formation of pearlite is infinitely slow at the A_1 temperature; that is, V equals and remains zero for an infinite period of time. According to the master charts of Fig. 1 this requires that $\lambda = 0$ for the A_1 temperature. Inasmuch as N/G must become finite for treatments at lower isothermal temperatures, λ changes with temperature.

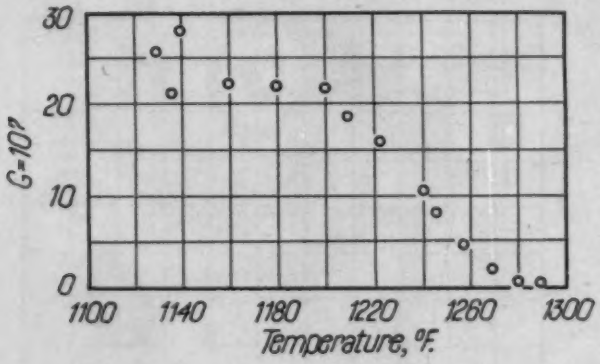

Fig. 8—Effect of Temperature on G.

Fig. 8 represents the variation of G with temperature. Near the pearlite nose of Bain's curve (1140 degrees Fahr.), G decreases gradually with an increase in temperature. As higher temperatures are reached the decline in G increases until 1280 degrees Fahr. (695 degrees Cent.) is reached. For yet higher temperatures G appears to remain a very small constant. What occurs as the A_1 temperature is reached was not completely investigated. Mehl (2) suggested that the growth rate of pearlite is a function of the interlamellar spacing of pearlite and the diffusivity of carbon in austenite. On the basis of these assumptions it was shown that the growth rate, G, changes with temperature according to:

$$\log G = A + \frac{B}{T},$$

where A and B are constants and T is the absolute temperature.

The present experimental work does not agree very well with Mehl's equation, the deviations from linearity of log G with respect to

$\frac{1}{T}$ being most pronounced near the nodular pearlite nose of Bain's curve and near the A_1 temperature. Over intermediate temperatures, however, Mehl's equation is not greatly in error. Evidently further investigations on interlamellar spacings at the extreme limits of the zone of pearlite formation are in order. It is further suggested that the interlamellar spacing may not be a function of the steel and its

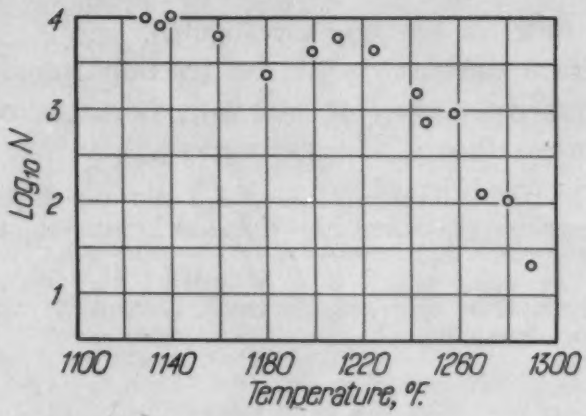

Fig. 9—Effect of Temperature on the Nucleation Constant.

temperature, but may also depend upon the diffusivity of the migrating atoms. Perhaps the interlamellar spacing diminishes with lower temperatures because the diffusivity is lower. Independent nucleation of ferrite and cementite would then demand that ferrite nucleate nearer the first cementite plate at lower temperatures, since the distance over which the carbon content is depleted, and the nucleation of ferrite thereby enhanced, is smaller. On the basis of this suggestion the interlamellar spacing becomes a function of the atomic diffusivity and the nucleation rates of ferrite and cementite. Consequently the nucleation rates of ferrite and cementite enter the expression for the growth rate of a pearlite nodule.

The influence of temperature on the nucleation constant, N, is represented in Fig. 9. For the greater portion of the region investigated, Log_{10} N has approximately the same variation with temperature as G. As the A_1 temperature is approached, however, log N continues to diminish unabated, indicating that at the A_1 N may approach zero; that is, no real nuclei mature into nodules. Comparison of the differences in N and G with temperature again points to the fact that the steel selected for the present study does not have an isokinetic rate of pearlite formation.

Summary

1. The Johnson-Mehl theory of pearlite formation was extended for application to nuclei counts at small percentages transformed (Fig. 3).

2. A method of determining the values of N, G, and λ by a single test was described and applied (Fig. 4).

3. It was found that for all practical purposes N and G are independent of time for the steel investigated.

4. Theoretical calculations of the fraction transformed from nucleation data agreed reasonably well with the experimental results. Deviations between theory and experiment, however, were noted above 65 per cent transformed.

5. The pearlite reaction for the steel investigated was not isokinetic.

6. The influence of temperature on λ, G, and N was determined and discussed.

Acknowledgments

The authors wish to acknowledge N. Y. A. assistance for the calculations which were required to establish the master charts in this paper.

References

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4. A. E. Flanigan, M.S. Thesis, University of California, 1940.
5. E. Scheil and A. Lange-Weise, *Arch. f. d. Eisenhüttenwesen,* Vol. 2, 1937, p. 93.
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TECHNICAL PROGRAM AND REPORTS OF OFFICERS AMERICAN SOCIETY FOR METALS—23rd ANNUAL CONVENTION, PHILADELPHIA, OCTOBER 20 to 24, 1941

FOR the benefit of members who were not in attendance at the Twenty-third Annual Convention of the Society, held in Philadelphia, October 20 to 24, 1941, and for purposes of record, the Technical Papers Program, the National Defense Group Meetings, and Reports of Officers presented at the annual meeting are herewith published in full.

TECHNICAL PAPERS PROGRAM

MONDAY, OCTOBER 20

Morning Session—Ballroom, Benjamin Franklin Hotel

Alloy Steels Session

Joint Chairmen—T. H. Wickenden and L. L. Wyman

The Nickel-Molybdenum System, by F. H. Ellinger, General Electric Co.

The Acicular Structure in Nickel-Molybdenum Cast Irons, by R. A. Flinn, American Brake Shoe & Foundry Co., Morris Cohen and John Chipman, Massachusetts Institute of Technology.

Elimination of the Apparent Hot Brittleness of 0.50 Molybdenum Steel, by C. L. Clark, Timken Roller Bearing Co., and J. W. Freeman, University of Michigan.

Some Properties of Phosphorus-Titanium Steels, by G. F. Comstock, The Titanium Alloy Mfg. Co.

Wear Tests on Ferrous Alloys, by O. W. Ellis, Ontario Research Foundation.

Morning Session—Washington Room, Benjamin Franklin Hotel

Fabrication Session

Joint Chairmen—H. E. Brown and S. Tour

The Effect of Microstructure Upon the Work Hardening Characteristics of a 0.74% Carbon Strip Steel, by N. P. Goss and Wm. Brenner, Jr., Cold Metal Process Co.

Problems in the Drawability of Deep Drawing Sheets, by M. Asimow, Central Metal Products Co., and J. N. Crombie, Carnegie-Illinois Steel Corp.

A Study of Cutting Oils With and Without Added Sulphur, by O. W. Boston, University of Michigan, and J. C. Zimmer, Standard Oil Development Co.

Some Properties of Sintered and Hot Pressed Copper-Zinc Powder Compacts, by C. G. Goetzel, American Electro Metal Corp.

Homogenization of Copper-Nickel Powder Alloys, by F. N. Rhines and R. A. Colton, Carnegie Institute of Technology.

Morning Session—Betsy Ross Room, Benjamin Franklin Hotel

Research Methods Session

Joint Chairmen—F. B. Foley and M. Gensamer

Magnetic Methods for Determining Carbon in Steel, by B. A. Rogers, Karl Wentzel and J. P. Riott, U. S. Bureau of Mines.

Application of Oscillograph to Determination of Cooling Rates of Quenched Steels, by C. R. Austin, Pennsylvania State College, R. M. Allen, Carnegie-Illinois Steel Corp., and W. G. Van Note, North Carolina State College.

The Influence of Alloying Elements on the Critical Points of Steels as Measured by the Dilatometer, by R. N. Gillmor, General Electric Co.

X-Ray Study of the A_3 Point of Pure Iron Using the Geiger-Muller Counter, by A. P. Wangsgard, University of Utah.

Heat Etching as a General Method for Revealing the Austenite Grain Size of Steels, by O. O. Miller and M. J. Day, United States Steel Corp.

Ballroom, Benjamin Franklin Hotel—11:30 A.M.

Non-Technical Talk on General Needs of National Defense, by Major General Jacob L. Devers, in Command of Armored Force, U. S. Army.

Ballroom, Convention Hall—2:30 P.M.

National Defense Group Meeting on *Low Carbon Alloy Steels (Case Hardening Steels);* see page 1042.

No. 300 Room, Convention Hall—5:00 P.M.

Educational Course on *Heat Flow in Metals,* by J. B. Austin, United States Steel Corp. Research Laboratories.

No. 400 Room, Convention Hall—8:00 P.M.

National Defense Group Meeting on *Manufacture of Shells;* see page 1042.

Ballroom, Convention Hall—8:00 P.M.

National Defense Group Meeting on *Problems in the Fabrication of Aluminum Base Alloys and Magnesium Base Alloys for Defense Material;* see page 1042.

No. 300 Room, Convention Hall—8:00 P.M.

Educational Course on *Hardness and Hardness Measurements,* by S. R. Williams, Amherst College.

TUESDAY, OCTOBER 21

Morning Session—Washington Room, Benjamin Franklin Hotel

Hardenability and Physical Properties Session

Joint Chairmen—W. J. Conley and T. G. Digges

Hardenability Testing of Low Carbon Steels, by R. C. Frerichs and E. S. Rowland, Timken Roller Bearing Co.

Hardenability of Shallow-Hardening Steels, by C. B. Post, O. V. Greene and W. H. Fenstermacher, Carpenter Steel Co.

The Effect of Carbon Content and Cooling Rate on the Decomposition of Austenite During Continuous Cooling of Plain Carbon Steels, by R. F. Thomson, Chrysler Corp., and C. A. Siebert, University of Michigan.

The Tensile Properties of Pearlite, Bainite and Spheroidite, by M. Gensamer, E. B. Pearsall, W. S. Pellini and J. R. Low, Jr., Carnegie Institute of Technology.

Effects of Initial Structure on Austenite Grain Formation and Coarsening, by M. Baeyertz, Carnegie-Illinois Steel Corp.

Morning Session—Ballroom, Benjamin Franklin Hotel

Corrosion and Stainless Steels Session

Joint Chairmen—C. W. Mason and A. W. Winston

The Influence of Stress on the Corrosion Pitting of Steel in Distilled Water, by D. J. McAdam, Jr., and G. W. Geil, National Bureau of Standards.

The Rate of Formation of Tin-Iron Alloy During Hot Dip Tinning as Measured by a Magnetic Method, by A. U. Seybolt, Battelle Memorial Institute.

The Role of Nitrogen in 18-8 Stainless Steel, by H. H. Uhlig, General Electric Co.

The Cyclic Temperature Acceleration of Strain in Heat Resisting Alloys, by G. R. Brophy and D. E. Furman, International Nickel Co.

Balancing the Composition of Cast 25% Chromium, 12% Nickel Type Alloys, by J. T. Gow and O. E. Harder, Battelle Memorial Institute.

Morning Session—Betsy Ross Room, Benjamin Franklin Hotel

Heat Treatment Session

Joint Chairmen—J. F. Wyzalek and J. F. Oesterle

Urea Process for Nitriding Steels, by R. P. Dunn, Electro Manganese Corp., W. B. F. Mackay, Royal Canadian Air Force, and R. L. Dowdell, University of Minnesota.

The Kinetics of Graphitization in White Cast Iron, by H. A. Schwartz, National Malleable and Steel Castings Co.

Effects of Small Amounts of Alloying Elements on Graphitization of Pure Hypereutectoid Steels, by C. R. Austin, Pennsylvania State College, and B. S. Norris, United States Pipe and Foundry Co.

Properties and Structures of Case Hardened Steels Affected by Cooling Practice After Carburizing, by O. W. McMullan, Youngstown Sheet and Tube Co.

The Precipitation Reaction in Aged Cold-Rolled Brasses: Its Effects on Hardness, Conductivity, and Tensile Properties, by R. H. Harrington and T. C. Jester, General Electric Co.

Ballroom, Benjamin Franklin Hotel—11:30 A.M.

Non-Technical Talk on *General Needs of National Defense,* by Lieutenant Commander J. C. Crommellin, Bureau of Aeronautics, U. S. Navy.

Ballroom, Convention Hall—2:30 P.M.

National Defense Group Meeting on *Higher Alloys Steels (Oil Quenching Steels);* see page 1043.

No. 400 Room, Convention Hall—2:30 P.M.

National Defense Group Meeting on *Copper and Its Alloys;* see page 1043.

No. 300 Room, Convention Hall—5:00 P.M.

Educational Course on *Heat Flow in Metals,* by J. B. Austin, United States Steel Corp. Research Laboratories.

Ballroom, Convention Hall—8:00 P.M.

National Defense Group Meeting on *Stainless and Heat Resisting Steel;* see page 1044.

No. 300 Room, Convention Hall—8:00 P.M.

Educational Course on *Hardness and Hardness Measurements,* by S. R. Williams, Amherst College.

WEDNESDAY, OCTOBER 22

9:30 A.M.—Ballroom, Benjamin Franklin Hotel

Annual Meeting of the American Society for Metals

Edward de Mille Campbell Memorial Lecture, by R. F. Mehl, Carnegie Institute of Technology. Chairman—Edgar C. Bain

Ballroom, Convention Hall—2:30 P.M.

National Defense Group Meeting on *High Strength Low Alloy Steels (Weldable Grades for Pressure Vessels, Piping, Ships, Rolling Stock);* see page 1044.

No. 300 Room, Convention Hall—5:00 P.M.

Educational Course on *Heat Flow in Metals,* by J. B. Austin, United States Steel Corp. Research Laboratories.

Ballroom, Convention Hall—8:00 P.M.

National Defense Group Meeting on *Inspection of Metals;* see page 1045.

No. 300 Room, Convention Hall—8:00 P.M.

Educational Course on *Hardness and Hardness Measurements,* by S. R. Williams, Amherst College.

THURSDAY, OCTOBER 23

Morning Session—Ballroom, Benjamin Franklin Hotel

Symposium on Controlled Atmospheres

Joint Chairmen—L. W. Kempf and E. G. Mahin

Fundamental Features of Controlled Atmospheres, Particularly for the Heat Treatment of Steel, by H. W. Gillett and B. W. Gonser, Battelle Memorial Institute.

Chemical Equilibrium as a Guide in the Control of Furnace Atmospheres, by J. B. Austin, United States Steel Corp., and M. J. Day, Carnegie-Illinois Steel Corp.

Prevention of Oxidation Type of Reaction of Ferrous Metals, by A. G. Hotchkiss and H. M. Webber, General Electric Co.

Prevention of Oxidation Type of Reaction in the Heat Treatment of Copper and Its Alloys, by E. G. deCoriolis and William Lehrer, Surface Combustion Corp.

The Heat Treatment of the Chromium-Carbon Stainless Steels, by W. E. Mahin and W. C. Troy, Westinghouse Electric & Mfg. Co.

Morning Session—Betsy Ross Room, Benjamin Franklin Hotel

Physical Properties Session

Joint Chairmen—J. J. Kanter and B. L. McCarthy

The Effect of Strain Rate Upon the Tensile Impact Strength of Some Metals, by E. R. Parker and C. Ferguson, General Electric Co.

Effect of Grain Size and Heat Treatment Upon Impact Toughness at Low Temperatures of Medium Carbon Forging Steel, by S. J. Rosenberg and D. H. Gagon, National Bureau of Standards.

Low Temperature Impact Resistant Steel Castings, by N. A. Ziegler and H. W. Northrup, Crane Co.

Dynamic Hardness Testing of Metals and Alloys at Elevated Temperatures, by Erich Fetz, C. O. Jelliff Mfg. Corp.

Morning Session—Washington Room, Benjamin Franklin Hotel

Metallography of Steel Session

Joint Chairmen—A. A. Bates and W. E. Benninghoff

Microstructural Characteristics of High Purity Alloys of Iron and Carbon, by T. G. Digges, National Bureau of Standards.

The Structure of Pearlite, by F. C. Hull, Westinghouse Electric & Mfg. Co., and R. F. Mehl, Carnegie Institute of Technology.

The Interlamellar Spacing of Pearlite, by G. E. Pellissier, International Nickel Co., M. F. Hawkes, Carnegie Institute of Technology, W. A. Johnson, Westinghouse Electric, and R. F. Mehl, Carnegie Institute of Technology.

The Martensite Thermal Arrest in Iron-Carbon Alloys and Plain Carbon Steels, by A. B. Greninger, General Electric Co.

A Study of Martensite Formation by a Photometric Method, by E. R. Saunders, Union Carbide & Carbon Corp., and J. F. Kahles, University of Cincinnati.

Ballroom, Benjamin Franklin Hotel—11:30 A.M.

General Needs of National Defense, by Rear Admiral Thomas T. Craven, U.S.N.

Ballroom, Convention Hall—2:30 P.M.

National Defense Group Meeting on *Alloy Castings (Steel and Iron);* see page 1045.

No. 300 Room, Convention Hall—2:30 P.M.

Defense Meeting on *Bearings: Problems, Conservation and Substitution;* see page 1046.

No. 300 Room, Convention Hall—5:00 P.M.

Educational Course on *Heat Flow in Metals,* by J. B. Austin, United States Steel Corp. Research Laboratories.

Ballroom, Benjamin Franklin Hotel—7:30 P.M.

Annual Banquet of the American Society for Metals

FRIDAY, OCTOBER 24

Morning Session—Ballroom, Benjamin Franklin Hotel

Symposium on Controlled Atmospheres

Joint Chairmen—E. H. Dix and H. C. Knerr

Prevention of Decarburization in Aircraft Engine Parts, by J. A. Comstock, Pratt & Whitney Aircraft Div.

Methods for Determining the Degree of Carburization or Decarburization and Evaluating Controlled Atmospheres, by N. K. Koebel, Lindberg Engineering Co.

Surface Effects Accompanying the Heating of Carbon Tool Steel in Oxidizing Atmospheres, by R. D. Stout and Toivo Aho, Lehigh University.

Discussion of Equipment, Instrumentation and Economy, by E. E. Slowter, Battelle Memorial Institute.

Atmospheric Control in the Heat Treatment of Aluminum Products, by P. T. Stroup, Aluminum Co. of America.

Atmospheric Control in the Heat Treatment of Magnesium Products, by C. E. Nelson, Dow Chemical Co.

Morning Session—Washington Room, Benjamin Franklin Hotel

High Speed Steels Session

Joint Chairmen—L. S. Bergen and W. J. Diederichs

Electrical Resistance Method for the Determination of Isothermal Austenite Transformations, by F. B. Rote, International Nickel Co., W. C. Truckenmiller, A-C Spark Plug Div., General Motors Corp., and W. P. Wood, University of Michigan.

The Tempering of Two High Carbon, High Vanadium High Speed Steels, by B. S. Lement and Morris Cohen, Massachusetts Institute of Technology.

The Transformation of Retained Austenite in High Speed Steel at Sub-Atmospheric Temperatures, by M. P. Gordon and Morris Cohen, Massachusetts Institute of Technology.

Study of Dimensional and Other Changes in Various Die Steels Due to Heat Treatment, by G. M. Butler, Jr., Allegheny Ludlum Steel Corp.

Hardening Characteristics of an Iron-Cobalt-Tungsten Alloy, by W. P. Sykes, General Electric Co.

Morning Session—Betsy Ross Room, Benjamin Franklin Hotel

Steel Making and Research Session

Joint Chairmen—A. O. Schaefer and W. M. Saunders, Jr.

The Over-All Linear Expansion of Three Face-Centered Cubic Metals (Al, Cu, Pb) From —190° C. to Near Their Melting Points, by J. W. Richards, Mt. St. Mary's College.

The Temperature and Manner of Growth of Shatter Cracks in Steel Rails, by H. B. Wishart and E. P. Epler, Carnegie-Illinois Steel Corp., and R. E. Cramer, University of Illinois.

The Carbon-Oxygen Equilibrium in Liquid Iron, by Shadburn Marshall, Remington Arms Co., and John Chipman, Massachusetts Institute of Technology.

The Solubility of Iron Oxide in Liquid Iron, by John Chipman, Massachusetts Institute of Technology, and K. L. Fetters, Carnegie Institute of Technology.

Rapid Temperature Measurements of Molten Iron and Steel With an Immersion Thermocouple, by Fulton Holtby, University of Minnesota.

Ballroom, Benjamin Franklin Hotel—11:30 A.M.

What Metal Industry Can Do to Help O.P.M., by Alex Taub, Technical Consultant to O.P.M.

Ballroom, Convention Hall—2:30 P.M.

National Defense Group Meeting on *Molybdenum High Speed Steels and Tool Steels;* see page 1046.

No. 300 Room, Convention Hall—5:00 P.M.

Educational Course on *Heat Flow in Metals,* by J. B. Austin, U. S. Steel Corp. Research Laboratories.

NATIONAL DEFENSE GROUP MEETINGS

MONDAY, OCTOBER 20

2:30 P.M.—Ballroom, Convention Hall

Low Carbon Alloy Steels (Case Hardening Steels)

Leader—Gordon T. Williams, Metallurgist, Deere & Co.

Summarizer—O. W. McMullan, Metallurgist, Youngstown Sheet & Tube Co.

Report from Conservation and Substitution Committee.

Commonly Used Alloy Steels That Are Scarce or Unobtainable, by Walter Hildorf, Chief Metallurgical Engineer, Timken Steel & Tube Co.

Suggestions About Substitutes That Will Not Run Into Other Bottlenecks, by E. T. Barron, Manager, Metallurgical Division, Pittsburgh District, Carnegie-Illinois Steel Corp.

Comparison of Scarce Steels and Substitutes as to Machinability, Speed of Carburization, Hardness of Case, Uniform Hardenability of Case, Strength and Toughness of Core, Nature of Quench, Amount of Distortion During Heat Treating, by F. E. McCleary, Metallurgical Engineer, Chrysler Corp.

Changes in Mechanical Design of a Part to Permit Substitutes, by Harry W. McQuaid, Consultant to OPM and Assistant Chief Metallurgist, Republic Steel Corp.

Open Discussion and Question Period.

Summary, by O. W. McMullan.

8:00 P.M.—No. 400 Room, Convention Hall

Manufacture of Shells

Leader—Arthur F. Macconochie, Head, Department of Mechanical Engineering, University of Virginia

Summarizer—Ernest E. Thum, Editor, METAL PROGRESS

Forged Shells, by F. G. Schranz, General Manager, Baldwin-Southwark Div.

Heat Treatment of Shells, by Col. H. H. Zornig, Office of Chief of Ordnance.

Machining of Shells, by Ben C. Brosheer, Associate Editor, *American Machinist.*

Cartridge Cases, by Alan Morris, Research Engineer, Bridgeport Brass Co.

Open Discussion and Question Period.

Summary, by Ernest E. Thum.

8:00 P.M.—Ballroom, Convention Hall

Problems in the Fabrication of Aluminum Base Alloys and Magnesium Base Alloys for Defense Material

Leader—E. H. Dix, Jr., Chief Metallurgist, Aluminum Co. of America

Summarizer—Harry Huester, Metallurgist, Reynolds Metals Co.

Aluminum Castings and Their Heat Treatment, by B. Clements, Metallurgist, Wright Aeronautical Corp.

Aluminum Forgings and Their Heat Treatment, by L. W. Davis, Chief Metallurgist, Forgings Division, Aluminum Co. of America.

Aluminum Structural Shapes and Sheet, and Their Heat Treatment, by T. W. Bossert, Assistant Chief Metallurgist, Fabricating Division, Aluminum Co. of America.

Welding of Aluminum, by G. O. Hoglund, Welding Engineer, Aluminum Co. of America.

Machining of Aluminum, by W. A. Dean, Research Metallurgist, Aluminum Co. of America.

Magnesium Castings, by Arthur W. Winston, Director, Metallurgical Department, Dow Chemical Co.

Open Discussion and Question Period.

Summary, by Harry Huester.

TUESDAY, OCTOBER 21

2:30 P.M.—Ballroom, Convention Hall

Higher Alloy Steels (Oil Quenching Steels)

Leader—M. A. Grossmann, Chief Metallurgist, Chicago District, Carnegie-Illinois Steel Corp.

Summarizer—Harry W. McQuaid, Consultant, OPM, and assistant Chief Metallurgist, Republic Steel Corp.

Report from Conservation and Substitution Committee, by C. H. Herty, Jr., Research Metallurgist Bethlehem Steel Co.

Outline of Function of Principal Alloys in Steel, by E. C. Bain, Assistant to the Vice-President, U. S. Steel Corp.

Commonly Used Alloy Steels That Are Scarce or Unobtainable, by H. W. McQuaid, Assistant Chief Metallurgist, Republic Steel Corp.

Standardization of Steel Specifications, by C. L. Warwick, Consultant, Government Conservation Board, Division of Purchases, OPM.

Suggestions About Substitutes That Will Not Run Into Other Bottlenecks, by M. J. R. Morris, Chief Metallurgical Engineer, Republic Steel Corp.

Evaluating the Hardenability of Steel, by Walter E. Jominy, Research Metallurgist, Chrysler Corp.

Comparison of Scarce Steels and Substitutes as to Availability and Cost, Machinability at Normal and High Hardness Levels, Physical Properties Obtainable, Heat Treating Schedule and Quenching Equipment and Distortion, by H. J. French, Manager, Alloy Steel and Iron Development, International Nickel Co., Inc.

Changes in Mechanical Design of a Part to Permit Substitution, by H. W. McQuaid, Assistant Chief Metallurgist, Republic Steel Corp.

Open Discussion and Question Period.

Summary, by H. W. McQuaid.

2:30 P.M.—No. 400 Room, Convention Hall

Copper and Its Alloys

Leader—Harry P. Croft, Assistant Director of Research, Cleveland Mill Division, Chase Brass & Copper Co.

Summarizer—Major Leslie S. Fletcher, Frankford Arsenal

Report from Conservation and Substitution Committee, by Ernest E. Thum, Editor, METAL PROGRESS.

Increasing Production by Elimination of Unnecessary Alloys, by D. K. Crampton, Director of Research, Chase Brass & Copper Co.

Standardization of Specifications, by C. L. Warwick, Consultant, Government Conservation Board, Division of Purchases, OPM.

Conservation of Copper by Use of Temporary Substitutes:

(a) *In Diversified Industry,* by W. B. Price, Chief Chemist and Metallurgist, Scovill Mfg. Co.

(b) *In the Electrical Industry,* by T. S. Fuller, Engineer of Materials, Schenectady Works Laboratory, General Electric Co.

(c) *In Communications Industry,* by Earle E. Schumacher, Bell Telephone Laboratories.

Copper and Its Alloys in Munitions Parts, by Lt. W. W. Culbertson, Frankford Arsenal.

Copper in Iron and Steel for Defense Work, by J. E. Jackson, Metallurgical Engineer, Copper Iron and Steel Development Association.

Open Discussion and Question Period.

Summary, by Major Leslie S. Fletcher.

8:00 P.M.—Ballroom, Convention Hall

Stainless and Heat Resisting Steel

Co-Chairman (Steel)—A. L. Feild, Director of Research, Rustless Iron and Steel Corp.

Co-Chairman (Corrosion)—Robert J. McKay, Chemical Engineer, International Nickel Co., Inc.

Report from Conservation and Substitution Committee, Ernest E. Thum, Editor, METAL PROGRESS.

The Problem of Conservation:

(a) *Substitutes for Decorative Uses,* by C. E. Heussner, Chrysler Corp.

(b) *Use of Alloys of Lower Chromium and/or Nickel.*

(1) *16% Cr, 1½% Ni,* by Stanley P. Watkins, Manager, Development Division, Rustless Iron and Steel Corp.

(2) *13% Cr Steels,* by R. A. Lincoln, Assistant Director of Research, Allegheny Ludlum Steel Corp.

(3) *Use of Reclaimed Scrap in Higher Carbon Analyses,* by Hubert A. Grove, Metallurgist, Alloy Steel Division, Republic Steel Corp.

(c) *Clad Materials,* by S. L. Hoyt, Technical Advisor, Battelle Memorial Institute.

(d) *Conservation of and Substitution for Heat Resisting Alloys,* by M. A. Hunter, Technical Staff, Driver-Harris Co.

The Problem of Substitution:

(a) *Lead,* by R. L. Hallett, Chief Chemist, National Lead Co.

(b) *Silicon Irons,* by D. E. Jack, General Sales Manager, Duriron Co., Inc.

(c) *Calorized Irons,* by B. J. Sayles, The Calorizing Co.

(d) *Silicon Cementation,* by Harry K. Ihrig, Director of Laboratories, Globe Steel Tubes Co.

(e) *Manganese, Copper, Aluminum and Silicon as Substitutes for Chromium and Nickel in Quasi-Stainless Steels,* by Russell Franks, Metallurgical Engineer, Union Carbide and Carbon Research Laboratories, Inc.

(f) *Silver and Platinum Lined Equipment,* by Fred E. Carter, Director of Research, Baker & Co.

Open Discussion and Question Period.

Summary, by Robert J. McKay.

WEDNESDAY, OCTOBER 22

2:30 P.M.—Ballroom, Convention Hall

High Strength Low Alloy Steels (Weldable Grades for Pressure Vessels, Piping, Ships, Rolling Stock)

Leader—Col. Glen F. Jenks, Ordnance Department, U. S. Army

Summarizer—Ernest E. Thum, Editor, METAL PROGRESS

(This discussion was confined to steels used as received from steel mills; the customer doing no heat treatment other than perhaps a stress relief.)

Report from Conservation and Substitution Committee, by John Johnston, Head, U. S. Steel Corp. Research Laboratory.

Alloys Available to Give Strength Without Heat Treatment, by A. B. Kinzel, Chief Metallurgist, Union Carbide and Carbon Research Laboratories, Inc.

Limits of Alloying Before Weldability Is Impaired, by Leon C. Bibber, Welding Engineer, Carnegie-Illinois Steel Corp.

Substitutes for Scarce Alloys, by B. D. Saklatwalla, Consultant, Alloys Development Corp.

Substitutions in Various Industries:

(a) *Railroad Rolling Stock,* by B. D. Saklatwalla, Consultant, Alloys Development Corp.

(b) *Pressure Vessels, Piping and Bolting,* by J. J. Kanter, Materials Research Engineer, Crane Co.
(c) *Large Forgings,* by F. B. Foley, Superintendent, Research Department, The Midvale Co.
(d) *Ships' Hulls,* by Paul D. Ffield, Materials Engineer, Bethlehem Steel Co., Shipbuilding Division.
(e) *Bridges and Building Skeletons,* by Jonathan Jones, Chief Engineer, Bethlehem Steel Co.

Welded Pipe and Pressure Vessel Linings, by Merrill A. Scheil, Research Metallurgist, A. O. Smith Corp.
Open Discussion and Question Period.
Summary, by Ernest E. Thum.

8:00 P.M.—Ballroom, Convention Hall

Inspection of Metals

Leader—John W. W. Sullivan, Head, Inspection Division, Cleveland Ordnance District
Summarizer—W. J. Jeffries, District Chief Engineer, Philadelphia Ordnance District

Principles of Inspection of Non-ferrous Materials, by Ernest E. Thum, Editor, METAL PROGRESS.
Principles of Inspection of Ferrous Materials, by Earl Blaine, Chief Inspector, E. G. Budd Mfg. Co.
Inspection of Aircraft Engine Materials, by E. S. Marks, Quality Engineer, Pratt & Whitney Aircraft Div.
Army Ordnance Inspection, by Brig. Gen. R. H. Somers, Ordnance Dept. U. S. Army.
Navy Ordnance Inspection, by Lieut. Com. C. A. Misson, U.S.N., Inspector of Ordnance, Midvale Co.
Marine Construction Inspection, by Capt. Ralph T. Hanson, U.S.N., Supervisor of Shipbuilding, Cramp Shipbuilding Co.
Training of Inspectors, by Capt. K. J. Soderberg, Civilian Personnel Division, Office of Chief of Ordnance, U.S.A.
Open Discussion and Question Period.
Summary, by W. J. Jeffries.

THURSDAY, OCTOBER 23

2:30 P.M.—Ballroom, Convention Hall

Alloy Castings (Steel and Iron)

Co-Chairman (Iron Castings)—A. L. Boegehold, Head, Metallurgical Department, Research Laboratories Division, General Motors Corp.
Co-Chairman (Steel Castings)—C. H. Lorig, Battelle Memorial Institute

Report from Conservation and Substitution Committee.
Function of Nickel, Chromium and Vanadium That Are Scarce, by A. W. Demmler, Metallurgical Engineer, Vanadium Corp. of America.
Function of Silicon, Titanium and Phosphorus That Are More Plentiful, by G. F. Comstock, Metallurgist, Titanium Alloy Mfg. Co.
Function of Copper That Is More Plentiful, by J. E. Jackson, Metallurgical Engineer, Copper Iron and Steel Development Association.
Function of Molybdenum, and Utilization of Classified Scrap and Alloy Pig Iron, by Victor Crosby, Foundry Engineer, Climax Molybdenum Corp.
Situation in Various Important Industries:
(a) *Automotive,* by H. S. Austin, Foundry Metallurgist, Buick Motor Car Div., General Motors Co.

(b) *Power,* by Norman L. Mochel, Metallurgical Engineer, Westinghouse Electric & Mfg. Co.
(c) *Chemical and Petroleum,* by Francis B. Foley, Superintendent, Research Department, The Midvale Co.
(d) *Agricultural Machinery,* by Hyman Bornstein, Chief Metallurgist, Deere & Co.

Open Discussion and Question Period.
Summary, by C. H. Lorig.

2:30 P.M.—No. 300 Room, Convention Hall

Bearings: Problems, Conservation and Substitution

Leader—O. E. Harder, Assistant Director, Battelle Memorial Institute
Summarizer—A. Allan Bates, Manager, Chemical and Metallurgical Department, Westinghouse Electric & Mfg. Co.

Report from Conservation and Substitution Committee.
Replacing Tin-Base Babbitts by Lead-Base Babbitts, by Carl E. Swartz, Metallurgist, Cleveland Graphite Bronze Co.
Bronze Bushings, by E. R. Darby, Director of Research, Federal Mogul Corp.
Problems and Substitutes in Powder Metallurgy Bearings, by R. P. Koehring, Metallurgist, Moraine Products Division, General Motors Corp.
Cadmium-Base Bearings, by C. F. Smart, Metallurgist, Pontiac Motor Division, General Motors Corp.
Silver Bearings, by E. A. Ryder, Consulting Engineer, Pratt & Whitney Aircraft Div.
Bearing Substitutes in the Automotive Industry, by Arthur F. Underwood, Head of the Mechanical Engineering Department, Research Laboratories Division, General Motors Corp.
Problems in Aircraft Bearings, by E. A. Ryder, Pratt & Whitney Aircraft Div.
The Use of Iron-Copper Bearings, by A. J. Langhammer, Amplex Division, Chrysler Corp.
Open Discussion and Question Period.
Summary, by A. Allan Bates.

FRIDAY, OCTOBER 24

2:30 P.M.—Ballroom, Convention Hall

Molybdenum High Speed Steels and Tool Steels

Leader—Bradley Stoughton, Chief, Heat Treating Equipment Unit, Tools Section, OPM
Summarizer—G. V. Luerssen, Metallurgist, Carpenter Steel Co.

Report on Alloying Elements from Conservation and Substitution Committee, J. P. Gill, Vanadium-Alloys Steel Co.
OPM Committee Report on the Heat Treatment of Molybdenum High Speed Steel:
(a) *Operations,* Norman I. Stotz, Metallurgist, Universal-Cyclops Steel Corp., Chairman.
(b) *Furnaces and Controlled Atmospheres,* Sam Tour, Vice-President, Lucius Pitkin, Inc.
(c) *Salt Baths,* A. F. Holden, President, A. F. Holden Co., Chairman.
Tool Steels, by James P. Gill, Chief Metallurgist, Vanadium-Alloys Steel Co.
Open Discussion and Question Period.
Summary, by G. V. Luerssen.

ANNUAL ADDRESS OF THE PRESIDENT

Twenty-third Annual Convention, Philadelphia, October 22, 1941

OSCAR E. HARDER, *President*

IT is a pleasure to report to you at this time that your Society has had an excellent year. This statement can be made on the basis of all of the activities in which the Society is engaged. Special mention may be made of educational activities, both in the chapters and on the part of the National Society.

The membership of the Society has reached a new high, the Western Metal Exposition and Congress made a new record, METAL PROGRESS is enjoying its best year from a business standpoint and has again received an award in Industrial Marketing's Annual Competition for Editorial Achievement, the present Exposition is the largest in history and the financial position of the Society has again improved. These items will be presented more in detail in the annual reports of your Secretary and Treasurer at this meeting. This continued success is due to individual members, chapter committees and officers, national committees, your board of trustees, and, in a large measure to your Secretary and his able staff at the National Office.

The Board of Trustees held four meetings during the year—November 15, 1940, May 20, 1941, August 8, 1941, and October 21, 1941. A detailed report of each of these meetings has been, or will be, published in the issue of THE REVIEW that followed. Your President takes this opportunity to acknowledge before the membership his debt of gratitude to the Trustees of the Society for the serious and whole-hearted interest they have shown in the trust which you have placed in them.

The Past President's medal was awarded to William P. Woodside at the Annual Banquet in Cleveland on October 24th, 1940.

There was no Henry Marion Howe Medal award in 1940.

The Board of Trustees reviewed the rules governing the award of the Henry Marion Howe Medal and made some changes as published in THE REVIEW for December, 1940. The papers to be considered for the 1941 award were divided into five groups which were reviewed by five committees of three men each, from which ten papers were selected for review by the Final Committee of five members. The award will be made at the banquet on Thursday evening.

The Campbell Memorial Lecture, established in 1925, was presented in 1940 by Dr. Samuel L. Hoyt, Battelle Memorial Institute, entitled "The Scientific Method in Metallurgy", and was published in the TRANSACTIONS for December 1940.

The Sauveur Achievement Award, established in 1934, was awarded at the Annual Meeting, 1940, to A. W. Machlet, in recognition of his achievement in metallurgical developments, and because Mr. Machlet was unable to be present, was received by P. C. Osterman who had been associated with Mr. Machlet for almost 40 years.

It is with deep regret that we report the death of one of our founder members, Theodore E. Barker, at Atascadero, California, on August 14th. Mr. Barker was elected to founder-membership due to the important part he played beginning in 1917, when he became the first chairman of the first organized movement to promote the science of metal treating in Chicago. He was twice chairman of the Chicago Chapter and served as a director of the Society in 1927 and 1928.

It is also with deep regret that we report the death of one of our Past Presidents, William S. Bidle, at his home in Cleveland on May 11th. He was a Charter member and Past Chairman of the Cleveland Chapter and President of the National Society 1924-1925.

The President's Bell was established in 1926 by President Bird to stimulate competition among the chapters. Later the emphasis was taken off of competition and the Bell was awarded by the President of the Society to the chapter which he felt had performed the most outstanding work in furthering the interests of the local chapter and the National Society.

It has become increasingly difficult for the President to make this award because of the excellent work of all of the chapters and of the difficulty or impossibility of visiting all of the chapters and having adequate information upon which to make a selection. Therefore, at the last meeting of the Board of Trustees the recommendation was made and accepted by the Board that inasmuch as the President's Bell has served the purpose for which it had been originally awarded that it should be retired from active service and placed in the Sauveur Memorial Museum at national headquarters.

The Board of Trustees felt, however, that the meritorious work of the chapters of the Society should be properly recognized and they have, therefore, ordered a replica of the bell to be cast and a

copy of the bell and a mallet to be sent, with a properly cast top showing the name of the chapter, to each chapter of the Society. These bells have been ordered and, as soon as they are received in the National Office, will be dispatched to the chapters.

It is of interest to record at this time that the President's Bell has been awarded to chapters as follows:

President's Bell was awarded as follows:
1926—Lehigh Valley
1927—Golden Gate
1928—Philadelphia
1929—Los Angeles
1930—New Jersey
1931—Hartford
1932—Montreal
1933—Cleveland
1934—Cleveland
1935—Chicago
1936—Peoria
1937—Philadelphia
1938—Los Angeles
1939—Cincinnati
1940—Texas

At the meeting a year ago, President Gill announced the action of the Board of Trustees in offering the full co-operation of all the members of your Society for national defense. It has been quite pleasing to your Officers to note the splendid manner in which A.S.M. has responded to the call of national defense. The chapter activities have been shaped toward that end and many chapters have held educational courses dealing with inspection and other metallurgical problems. Not only have the educational activities been along the lines of defense but they have been greatly increased and accelerated.

The Society has been pleased to co-operate with O.P.M. and other Government agencies in the formation of committees and preparation of reports. Your National Secretary, W. H. Eisenman, is Secretary of the Metals Conservation and Substitution Group of the Committee on Minerals of the National Research Council. The number of members of the Society who are serving in positions of responsibility both in consulting lines and in actual direction of activities has been observed with a great deal of pride.

As you have noted, the National Metal Congress and Exposition year has streamlined other activities so that more attention is focused upon the problems of defense, conservation and substitution. I am sure that the new Board of Trustees will stand ready to put

forward all the abilities and facilities of the Society in the interest of national defense.

Announcement was made by President Gill last year of a co-operative project between A.S.M. and the Ohio State University Research Foundation to study "Methods of Visual Education". This project was handicapped somewhat by some of the Ohio State University staff members being called into defense work but the work outlined for the first year has now been completed and a movie of over 600 feet on the subject of "Metal Crystals" has been developed. This movie has been highly commended by members of the Educational Committees who have seen it and it will be available for use by the various chapters during the coming year. It seems likely that further work along this line will be authorized by the Board of Trustees at later meetings. Thanks are due to the Educational Committee for the active interest they have taken in this project and to the members of the staff of Ohio State University who have conducted the work.

During the current year your President, by traveling some twenty thousand miles, has visited thirty chapters, met with the officers and members of the executive committees of these chapters, and given technical talks to twenty-seven of them. It was his good fortune to have your Secretary, W. H. Eisenman, with him on a number of these visits which was very pleasant and helpful. Unfortunately, the demands in connection with the Western Metal Exposition and Congress made it impossible for him to be present on a number of these visits and his presence was seriously missed by your President and by the chapters.

The status of the chapters, as indicated by those visited, is very fine indeed. They are interested in their own chapter activities and in the activities of the National Society. There is a general trend for increased service to the members and to the industries which they represent. Most of the chapters are conducting educational courses and some of the larger chapters have rather extensive educational programs. Other activities in which the chapters are engaged include vocational guidance to seniors from the high schools, assistance in employment service, and now some of the chapters have established special committees to work on defense problems, conservation of strategic and critical materials, the use of substitute materials, and the collection and dissemination of the best processes in production. Considerable satisfaction results from a visit to the

Southern chapter which, within its first year, has conducted two successful educational courses.

Our Society is under deep obligation to the men who are presenting two series of educational lectures during this Convention.

Dr. J. B. Austin, physical chemist, U. S. Steel Corporation Research Laboratory, is presenting a series of five afternoon lectures on the subject "Heat Flow in Metals" and if Dr. Austin will be kind enough to come forward, I wish to present to him, on behalf of the Society, a certificate of appreciation for his lectures.

Professor R. S. Williams, Professor of Physics, Amherst College, is presenting a series of three evening educational lectures on "Hardness and Hardness Measurements", and if Professor Williams will be kind enough to come forward I wish to present to him, on behalf of the Society, a certificate of appreciation for his lectures.

On behalf of the American Society for Metals, it is my pleasure to express our great appreciation to the co-operating societies which have participated in the National Metal Exposition and the National Metal Congress. The Iron and Steel Division and the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, The American Welding Society, and the Wire Association, have contributed valuable parts.

Our thanks are also due to the authors of the technical papers on the programs of the American Society for Metals and of the co-operating societies.

Special thanks are due to those who on short notice have taken part in the series of meetings on the defense problems, conservation and substitutions, and for the co-operation of men from the War and Navy Department and O.P.M. in the series of defense meetings being held at 11:30 on Monday, Tuesday, Thursday and Friday.

Our sincere thanks are extended to the exhibitors in this the 23rd National Metal Exposition which is the largest in history. Not only have these exhibitors displayed their products and processes but they have co-operated with the theme of this Exposition and Congress and have emphasized how they will aid in defense production, conservation of strategic and critical materials and in possible substitutions. We greatly appreciate the co-operation of the more than three hundred and fifty exhibitors.

In conclusion, I wish to express my personal appreciation for the fine co-operation which has been received from so many members of the Society, officers of the chapters, members of national

committees, the national officers, all of which has made it a pleasant experience to serve your Society. I can only wish for your incoming officers this continued co-operation and support, which I am sure they will have, and the continued success and growth of your Society.

REPORT OF THE TREASURER

KENT R. VAN HORN, *Treasurer*

The fiscal year, ending on August 31, 1941, has been another successful year in the history of the Society, and it is a pleasure for your Treasurer to submit this report.

Our cash balance on August 31, 1941, was $144,754.67 against last year's $120,591.07. We are, therefore, in a very liquid position and can take advantage of any opportunities or of a drastically depressed market.

Security holdings of the Society increased the past year from $199,744.34 to $242,590.42, or 21.5 per cent. Several investments were called for redemption; but additional purchases replaced these holdings, and surplus funds permitted additional investments to be made. Total assets increased 13.2 per cent; deferred income and expense on the present Convention will, however, when the show accounts are complete, reduce the increase to approximately 10 per cent.

Our accounts receivable increased in total from $10,546.55 to $13,841.54, reflecting an increase in volume of business transacted, but still showing a very healthy condition of receivables which have an average collection period of less than 30 days.

Inventories have remained about the same, increasing $1,675.00 because of the publication of several new books and additional paper stock purchased at the end of the fiscal year. The office furniture and equipment account has increased approximately $2,000.00 from the purchase of additional floor coverings and equipment for the new office.

The investment in the headquarters building was increased by weatherstripping of windows, etc., but amortization of $1,650.00 has reduced carrying value to approximately $50,000.00.

The Finance Committee has been in constant touch with the A.S.M. fiscal agents, the Cleveland Trust Company, and a close contact with the investment market has been maintained. Addition of

top grade stocks to the portfolio during the present year has increased the hedge against inflation, will help to maintain dollar value, and has increased the diversification. A substantial investment in U. S. Government Defense Bonds has also been made.

The distribution of the investment portfolio is as follows:

		Per Cent
Real Estate (Headquarters)	$ 50,735.00	17.4
U. S. Gov't Bonds	32,500.00	11.1
Railroad Bonds	35,915.00	12.4
Public Utility Bonds	45,970.00	15.8
Industrial & Misc. Bonds	10,640.00	3.7
Common Stocks	115,180.00	39.6

Including the cash on hand, common stocks now represent 36.4 per cent of the investments. As of August 31, 1941, the total cost of present investments (not including Headquarters) was $242,-590.42, and the market value was $205,963.60. From 1921 to August 31, 1941, the investments have yielded $111,028.28 and the sale of securities during this period has resulted in an appreciation of $6,377.30.

The present market values of securities	$205,963.60
and Headquarters	50,734.77
Plus cash on hand	144,754.67
	$401,453.04

This total exceeds by only $48,000.00 the total operating cost of the Society and its activities for 1940-41, $353,378.86. The interest at 3 per cent that could be realized from this sum of $401,453.04 is, therefore, approximately only 3.5 per cent of the total operating expense (Society and Convention). The Finance Committee believes it is advisable to strive to maintain a substantial reserve.

The statement of income and expense for the year ending August 31, 1941, is as follows in total:

Income	$449,943.35	
Expense	353,378.86	
Excess		$96,564.49

Income from METAL PROGRESS increased approximately 21.4 per cent this year over the prior year from $119,433.00 to $145,-021.04, and expense increased 26.5 per cent from $108,302.06 to $125,875.03. The excess over expenses was $19,146.01 compared to $11,130.94 for 1940. The income from METAL PROGRESS now constitutes about one-third of the annual income.

TRANSACTIONS and THE REVIEW are, of course, not self-sustaining and cost the Society a net sum of approximately $19,620.00 and $4,580.00.

Miscellaneous items such as reprints, books purchased for resale, pins and buttons, automobile emblems, etc., balance out. For books published, however, there is an excess of approximately $13,900.00. This is attributable to the large increase in the number of volumes sold in spite of the recent policy of offering publications to the membership at reduced prices on publication and at certain intervals.

The 1939 edition of the METALS HANDBOOK continues as a best seller, and sales of $11,670.00 for the past year have been added to sales previously reported of $14,700.00.

The 1940 Convention and Exposition, as usual, was an outstanding event in the metal industry and was successful, not only financially, but artistically, as a selling and advertising medium for our exhibitors. The Western Metal Congress in Los Angeles in May registered a small excess of income over expenditures and brought to the West Coast members and industry many advantages of the National Exhibition.

The revenue from membership dues reached a new high this last fiscal year.

Gross total for	1941	$131,471.56
	1940	115,502.00
	1939	108,000.00
	1938	103,600.00
	1937	105,600.00

The 1941 income from membership represents 29.2 per cent of the total income; $52,536.69 of this income from membership was returned to the chapters. If this amount is deducted, membership dues contribute only 19 per cent to the general income.

The chapters now report assets, in addition to those of the National Office, totaling $92,600.00, an increase of $12,000.00 to the net worth reported a year ago. This reserve substantially insures the continued activity and progress of the chapters.

Your Treasurer gratefully acknowledges the active co-operation and assistance of the Finance Committee, Dr. Zay Jeffries—senior member of this committee, Secretary Eisenman, and Mr. C. W. Ohlson.

CONDENSED AUDITED BALANCE SHEET

As of August 31, 1941

ASSETS	
Cash	$144,754.67
Securities	203,477.91
Accounts receivable	13,841.54
Inventories	38,438.14
Other assets	2,575.66
Real estate	50,734.77
Office furniture, fixtures and equipment	14,220.04
Deferred charges	21,261.48
	$489,304.21
LIABILITIES AND SURPLUS	
Accounts payable	$ 12,125.16
Accrued taxes	2,294.55
Reserves	120,000.00
Deferred income	35,946.00
Surplus	318,938.50
	$489,304.21

INCOME AND EXPENSE STATEMENT

Year Ended August 31, 1941

INCOME		
METAL PROGRESS—monthly publication	$145,021.04	
Memberships	85,870.39	
1940 Convention—Cleveland	110,343.19	
Western Metal Show	40,702.18	
TRANSACTIONS	4,446.80	$386,383.60
Books published		35,356.31
National Metals Handbook—sales		11,666.88
Interest and dividends		8,334.62
General reprints		4,253.57
Discount earned		2,467.01
Rental income—charged to 1940 Convention		2,125.00
Books purchased for resale		416.20
THE REVIEW—advertising and subscriptions		74.29
Profit on disposal of securities—net		10.69
Sundry		980.18
TOTAL INCOME		$452,068.35
EXPENSES		
Metal Progress	$125,875.03	
Memberships	9,792.85	
1940 Convention—Cleveland	79,258.82	
Western Metal Show	30,957.91	
TRANSACTIONS	23,124.01	
Books published	21,451.14	
National Metals Handbook	7,373.98	
THE REVIEW	4,579.20	
General expenses	14,229.36	
Secretary's office	12,558.50	
Accounting department	7,465.04	
Headquarters	5,903.33	
National committees	1,654.53	
Expenses of trustees	1,622.63	
Expenses of President	1,414.53	
General reprints	3,678.03	
Books purchased for resale	387.96	
Research	3,301.15	
Lectures	520.00	
Medal fund expenses	102.77	
Books for library	192.68	
Sundry	60.41	
TOTAL EXPENSES		$355,503.86
NET INCOME BEFORE SURPLUS CHARGES		$ 96,564.49

OPINION

In our opinion, subject to the comments in the preceding paragraphs relative to income from investments and reserves, the accompanying balance sheet and related statements of income and surplus present fairly the position of the American Society for Metals at August 31, 1941, and the results of its operations for the year, in conformity with generally accepted accounting principles applied on a basis consistent with that of the preceding year.

ERNST & ERNST
Certified Public Accountants

ANNUAL REPORT OF THE SECRETARY

WILLIAM H. EISENMAN, *Secretary*

The American Society for Metals on October 1, 1941 had a total membership of 12,684. Of this number 11,123 or 87.6 per cent were the member classification; 750 or 5.9 per cent were sustaining members; while 790 or 6.3 per cent were juniors. There are 21 honorary and founder members.

On October 1, 1940, the Society had a total membership of 11,122. The membership this year showed a gain of 14 per cent.

Publication Committee

The Publication Committee for the year 1940-41 was made up of the following: L. W. Kempf, Chairman; L. S. Bergen, T. G. Digges, E. H. Dix, Jr., Maxwell Gensamer, J. J. Kanter, E. G. Mahin, B. L. McCarthy, M. J. R. Morris, J. F. Oesterle, Sam Tour, J. P. Walsted, A. W. Winston, L. L. Wyman, J. F. Wyzalek, and Ray T. Bayless, Secretary.

Throughout the year and up to the present time the Committee has reviewed and approved 59 papers, rejected 3, and is in the process of reviewing 5 at the present time.

The last meeting of the Publication Committee was held in National headquarters office in Cleveland on August 15 and 16, 1941. This meeting was concerned with the final approval of technical papers submitted for the Convention and with the scheduling of these papers on the technical program for this Convention.

Transactions

There has been published, since the last annual meeting of the Society, four quarterly issues of TRANSACTIONS, i.e. December 1940, March, June and September 1941. The number of pages published in these four issues totals 1074. There were 43 articles printed together with the discussions. A total of 49,481 TRANSACTIONS has been distributed to the membership during that period.

The TRANSACTIONS published since December 1940 contain papers presented at the 1940 Convention together with others received during the year.

Metal Progress

METAL PROGRESS, during the fiscal year, broke several of its previous praiseworthy records. The numbers of copies circulated topped 1940 by 11 per cent. Editorial pages in number totaled 645—the total number of revenue advertising pages reached the unprecedented figure of 1078 (up 18 per cent from 1940 fiscal).

Fiscal 1942 has started out in a manner which presages even higher levels of production. The annual reference issue, printed and mailed prior to this meeting, is the largest ever to be published by the American Society for Metals both in advertising and in editorial content.

Owing to the war in Europe, the well-read department "Foreign Correspondence" has had to be abandoned. However, the Editor's diary, printed under the heading "Critical Points", has appeared each month, and has won widespread favorable comment. A new business feature appeared in the January issue, and again six months later. It is in effect a metallurgical catalog, or "Where to Buy It" directory, and appears to be of enough importance in these changing times to warrant revision at six-months intervals.

For the fourth year in succession METAL PROGRESS has received one of the coveted awards in the competition conducted by Industrial Marketing and sponsored by the National Industrial Advertisers Association. These competitions embrace the entire trade and business press in America. The 1941 award for editorial achievement comprised a "Special Award to METAL PROGRESS for the best typographical excellence maintained during the year ending July 31, 1941".

It gives me pleasure to compliment the editorial and business staffs of METAL PROGRESS on these records. The thanks of the Society are also due to those hundreds of members who have submitted editorial matter of great excellence.

Preprints

Fifty-eight papers were presented before the 22nd annual Convention held in Cleveland last year, 55 of which were preprinted. For this year's Convention in Philadelphia, 60 papers have been scheduled for presentation, 55 of which have been preprinted and distributed to those members requesting them. The total number of

pages for 1941 is 1472. A total of 52,010 preprints have been distributed free to the membership to date.

Books

Since the last Convention, five books have been published and made available to members of the Society and others, i.e., "Metal—Inside Out", a series of six lectures presented by members of the Philadelphia Chapter and edited by Ray T. Bayless; "Strength of Metals Under Combined Stresses" by Dr. Maxwell Gensamer, a series of educational lectures presented at the 1940 Convention; "Inspection of Metals" by H. B. Pulsifer; "Surface Treatment of Metals", the 1940 symposium; "Visual Examination of Steel" by G. M. Enos, a series of three educational lectures presented at the 1939 Convention.

The following books are now in the process of preparation: "What Steel Shall I Use" by G. T. Williams; "Alloy Constructional Steels" by H. J. French; book on "Powder Metallurgy", edited by John Wulff which consists of papers presented at the conferences on powder metallurgy held at Massachusetts Institute of Technology in 1940 and 1941; the five-lecture series on "Heat Flow in Metals" which is being presented at the 1941 Convention by J. B. Austin and which will be ready for distribution shortly after the Convention. A book on "Hardness and Hardness Measurements" by S. R. Williams is in process of publication.

The Review

During the past year THE REVIEW has been published monthly with the exception of July and September. Of the 10 issues which appeared from November 1940 to October 1941 all contained 8 pages with the exception of the October 1941 issue which carried 16 pages.

The October issue was devoted almost entirely to the National Metal Congress and Exposition and had a circulation of 40,000 among the members of the co-operating societies in the Congress and other technical organizations.

Of the total space used in the 10 issues during the past year, 3722 column-inches or 84.6 per cent was devoted to editorial matter, and 678 column-inches or 15.4 per cent to advertising. Reports of chapter meetings and educational activities used 2069 column-inches or 47 per cent of the total space.

METALS HANDBOOK

The personnel of METALS HANDBOOK Committee is as follows:

R. S. Archer, Chairman, Republic Steel Corp.
E. C. Bain. United States Steel Corp.
W. P. Eddy, Jr., General Motors Truck & Coach
H. L. Maxwell (A.W.S. Rept.), E. I. duPont deNemours & Co.
R. F. Mehl, Carnegie Institute of Technology
H. D. Newell, Babcock & Wilcox Co.
C. W. Obert (I.A.A. Rept.), Union Carbide & Carbon Corp.
H. B. Pulsifer, American Metal Treating Co.
S. C. Spalding, American Brass Co.
A. P. Spooner, Bethlehem Steel Co.
N. I. Stotz, Universal-Cyclops Steel Co.
Lyall Zickrick (A.I.M.E. Rept.), General Electric Co.

The following men have very willingly given considerable of their time and assistance to METALS HANDBOOK activities. Their membership terms expired at the end of last year so have been retired from METALS HANDBOOK Committee membership. Their untiring services on the committee are appreciated by all:

E. L. Bartholomew, United Shoe Machinery Corp.
A. D. Beeken, Jr., Vulcan Crucible Steel Co.
A. O. Schaefer, Midvale Co.

METALS HANDBOOK Committee has made a very careful study of the contents and arrangement of METALS HANDBOOK. A number of major changes are in process for a complete revision and reorganization of certain HANDBOOK sections. Many new subcommittees and authors have been appointed to assist in this program.

One of the major changes is to reorganize the sections dealing with testing. A new section on mechanical testing is to be incorporated. In this section will be included short, concise articles on all of the important methods of mechanical testing including the present articles on these subjects in the present edition but after they have been revised and reorganized according to a specific plan and outline.

Another major undertaking is the closer control and supervision, by a special committee, of the articles on alloying elements. It is the plan to thoroughly revise and supervise these articles and enlarge upon them if necessary, as well as expand the section by adding other pertinent articles on the subject, so that the latest and best information will be given on the alloying, properties, and application of the important alloying elements.

Another important project for revising and reorganizing sections of the HANDBOOK is a program to bring all constitutional articles under the supervision of one committee so that uniformity and accuracy in all articles can be maintained, and brevity adhered to. All

articles on constitutional subjects are to be prepared according to a specific outline. This outline eliminates such information as mechanical properties and historical data, which belongs in other sections of the HANDBOOK and controls the number and quality of references selected. The constitutional articles are to be all arranged alphabetically in a special section instead of a number of specific sections as at present.

The new subjects that have been assigned, by METALS HANDBOOK Committee, for preparation by subcommittees and authors are as follows:

Alloying Elements—Subcommittee on Alloying Elements
- Master Property Chart—E. C. Bain
- Softening Curves—A. J. Herzig
- Hardenability of Alloy Steels—M. A. Grossmann
- S-Curves—E. S. Davenport

Conditioning of Semi-Finished Steel—(completed)—Prepared by subcommittee.

Constitutional Diagrams—Subcommittee on Constitutional Diagrams
(Many new articles will be added later to this section)

Cladding—Subcommittee on Cladding

Definitions—Subcommittee on Definitions

Properties of Forgings in Heavy Sections—Subcommittee on Forgings

Hardenability Tests—Subcommittee on Hardenability

Mechanical Testing—Subcommittee on Mechanical Testing
- Calibration of Testing Apparatus—Bruce L. Wilson
- Testing Castings—A. A. Bates
- Compression Tests—M. F. Sayre
- Creep Tests of Metals—J. J. Kanter
- Fatigue and Corrosion Fatigue—H. F. Moore
- Testing Forgings—A. O. Schaefer
- Hardness Testing—H. L. Scott
- Introduction to Mechanical Testing—R. L. Templin
- Notch Bar Testing—S. L. Hoyt
- Testing Plate, Shapes, and Bars—A. P. Spooner
- Testing Pressure Vessels—E. C. Wright
- Testing Rod and Wire—J. N. Low and M. Gensamer
- Testing Sheet and Strip—J. N. Low and M. Gensamer
- Test Specimens; Preparation of—R. L. Templin
- Tensile Testing—M. Gensamer
- Torsion Testing—G. V. Luerssen and O. V. Greene
- Testing Tubular Products—E. C. Wright
- Testing Welds—R. W. Emerson

Oxidizability of Metals and Alloys; Relative—Howard Scott

Pickling, Cleaning and Passivating of Stainless Steel—M. J. R. Morris

Powder Metallurgy—Subcommittee on Powder Metallurgy

Behavior of Metals Under Static Loads

Specifications—Subcommittee on Specifications
(Concise compilation of the properties in various metal specifications)

Tool Steel—Subcommttee on Tool Steel
- Forging, Normalizing and Annealing Tool Steels
- Cyaniding (nitriding) High Speed Steel at 1050 Degrees Fahr.
- Selection of Tool Steels

Welding and Cutting—Subcommittee on Welding and Cutting

The personnel of the METALS HANDBOOK Subcommittees that are working on these various projects are as follows:

A.S.M. Metals Handbook Subcommittees

As of October 1, 1941

Subcommittee on Alloying Elements
Prof. Bradley Stoughton, Chairman
R. D. Allen
E. C. Bain
A. A. Bates
A. L. Boegehold
Walter Crafts
D. L. Edlund
C. H. Herty
A. J. Herzig
H. B. Knowlton
J. W. Sands
C. E. Sims

Subcommittee on Constitutional Diagrams
K. R. Van Horn, Chairman
J. S. Marsh
F. N. Rhines

Subcommittee on Conditioning Semi-Finished Steel
(This article is now completed)
J. H. Flaherty, Chairman
J. R. Anderson
A. C. Badger
A. P. Spooner
H. J. Wiegal

Subcommittee on Cladding
S. L. Hoyt, Chairman
L. C. Grimshaw
E. H. Hill
R. A. Lincoln
E. E. Schumacher
L. C. Whitney

Subcommittee on Properties of Forgings in Heavy Sections
Jerome Strauss, Chairman
N. L. Mochel
A. O. Schaefer
S. H. Weaver

Subcommittee on Definitions
R. F. Mehl, Chairman
R. H. Aborn
V. O. Homerberg

Subcommittee on Mechanical Testing
A. O. Schaefer, Chairman
M. Gensamer
R. L. Templin
E. C. Wright

Subcommittee on Specifications
J. J. Crowe, Chairman
H. E. Landis, Jr.
F. C. Saacke

Subcommittee on Hardenability
M. A. Grossmann, Chairman
J. L. Burns
W. E. Jominy
G. V. Luerssen
G. C. Riegel
Reinhold Schempp
Gordon Williams

Subcommittee on Powder Metallurgy
Charles Hardy, Chairman
C. W. Balke
R. P. Koehring
L. L. Wyman

Subcommittee on Tool Steels
S. C. Spalding, Chairman
W. L. Badger
G. E. Brumbach
W. R. Frazer
J. H. McCadie
Reinhold Schempp
A. G. Spencer
A. P. Spooner
N. I. Stotz
W. H. Wills

Welding and Cutting

The International Acetylene Association has for a number of years co-operated with METALS HANDBOOK Committee and has had prepared by a special committee the sections in METALS HANDBOOK on welding and cutting. This splendid co-operation is deeply appreciated, and we are happy to report that the association will again supervise those two sections in METALS HANDBOOK. The committee appointed by the International Acetylene Association is as follows and we are pleased to report it is again under the able leadership of C. W. Obert.

Subcommittee on Welding and Cutting
(Special Committee appointed by the International Acetylene Association)

C. W. Obert, Chairman
C. L. Altenburger
R. W. Clark
E. V. David
C. H. Jennings
H. L. Maxwell
H. R. Morrison
E. W. P. Smith

Nonferrous Section

The Nonferrous Data Sheet Committee of the Institute of Metals Division of the A.I.M.E. is again planning and organizing the nonferrous section of METALS HANDBOOK. The committee has been very active in working out the various programs for the several divisions of the nonferrous sections. The personnel of the present committee is as follows and will this year again be under the efficient management of Lyall Zickrick:

Lyall Zickrick, Chairman, General Electric Co.
W. H. Bassett, Jr., Anaconda Wire and Cable Co.
E. W. Palmer, American Brass Co.
S. Skowronski, Raritan Copper Works
K. R. Van Horn, Aluminum Company of America
T. A. Wright, Lucius Pitkin, Inc.

The nonferrous subjects that have been assigned either to authors or subcommittees for preparation are as follows:

Aging and Age Hardening of Nonferrous Metals—Subcommittee on Aging
Bright Annealing and Atmosphere Controlled Furnaces—Subcommittee on Bright Annealing
Bolts, Screws and Nuts; Nonferrous—W. A. Straw
Bearing Metals—Subcommittee on Bearing Metals
Corrosion Properties of Nonferrous Metal—H. E. Haring
Coloring of Copper and Copper Alloys—C. B. F. Young
Conductivity of Copper—L. L. Wyman
Corrosion Resistant Lead Equipment in Industry; Use of—F. E. Wormser

Copper Alloys, Hot and Cold Working—Subcommittee on Hot and Cold Working of Copper Alloys
Magnesium Alloys for Forging, Sheets and Extrusion—Subcommittee on Magnesium
Magnesium Alloys; Principles of Design and Engineering, Application of—Subcommittee on Magnesium
Metals, Prices of
Pickling and Cleaning of Nonferrous Metal—Subcommittee on Pickling and Cleaning
Silver; Physical Properties of—A. J. Dornblatt
Copper Alloys, High Strength-High Conductivity—(completed)—Subcommittee on High Strength-High Conductivity Copper Alloys

The personnel of the Nonferrous Data Sheet Subcommittees that have been organized to prepare some of the above reports are as follows:

Subcommittee on Aging and Age Hardening of Nonferrous Metals
W. L. Fink, Chairman
C. S. Smith
W. P. Sykes

Subcommittee on Bright Annealing and Atmosphere Controlled Furnaces
R. M. Cherry, Chairman
Wm. Lehrer
P. E. Petersen

Subcommittee on Pickling and Cleaning of Nonferrous Metals
C. Dantsizen, Chairman
R. J. Wheeler

Subcommittee on Magnesium
A. W. Winston, Chairman
H. W. Schmidt
R. T. Wood

Subcommittee on Bearing Metals
O. W. Ellis, Chairman
C. E. Swartz
A. F. Underwood

Subcommittee on High Strength-High Conductivity Alloys
(This article is completed)
W. R. Hibbard, Chairman
P. H. Brace
H. L. Burghoff

Subcommittee on Hot and Cold Working of Copper Alloys
R. S. Pratt, Chairman
W. R. Hibbard

Handbooks

The Society has in stock 4445 HANDBOOKS. During the last year 4029 HANDBOOKS have been issued or an average of 336 books per month. To junior members or non-members of the society, 1055 of these HANDBOOKS have been sold, leaving 2974 HANDBOOKS issued to members of the society during the last year.

Educational Committee

The Educational Committee for the year 1941 was made up of the following: W. J. Conley, Chairman; A. A. Bates, H. C. Knerr, C. W. Mason, B. R. Queneau, W. M. Saunders, Jr., T. H. Wickenden and Ray T. Bayless, Secretary.

The Committee has held two meetings since the last Convention; one in Columbus, Ohio, on November 8, 1940, and the other in New York City, on September 5, 1941.

The meeting on November 8 was held at Ohio State University for the purpose of discussing with the members of the Research Foundation staff the production of the moving picture film "Metallic Crystals", and the details for the production of the film were carefully outlined. During this same meeting the two lecture courses which are being presented at this Convention were selected and the authors invited. These lectures are: The five-lecture series by J. B. Austin of U. S. Steel Corp. on "Heat Flow in Metals", and the three-lecture series on "Hardness and Hardness Measurements" by S. R. Williams of Amherst College, and are enjoying a very splendid attendance by members here at the Convention.

The meeting on September 5 concerned itself with the final aspects of the production of the moving picture film at Ohio State University, which has now been completed, and for the purpose of discussing the work of the Committee for the coming year. The Committee also decided upon a lecture course on "Spectroscopy" by Dr. E. J. Martin of General Motors Corporation for the 1942 Convention, and likewise discussed other lecture subjects but did not arrive at a selection during this meeting.

Western Metal Exposition and Western Metal Congress

The fourth Western Metal Congress and Exposition was held in Los Angeles the week of May 19, and proved to be outstandingly successful.

135 exhibitors participated, occupying a total of 35,000 square feet in the Pan-Pacific Auditorium.

The Western Metal Congress, a joint meeting of 18 of the national technical societies with representation on the Pacific coast, gathered together under the auspices of the American Society for Metals and the American Welding Society, provided a technical program of outstanding merit and possessing a great degree of unusualness.

The entire activity was indeed gratifying to the officers and trustees of the Society.

National Metal Congress and National Metal Exposition

It is rather difficult to raise record after record because one soon reaches a point beyond which the theory of limits is in effect.

The Exposition in Cleveland last year, with 103,000 square feet, marked an all-time high during twenty-two years of continuous displays.

However, it was left for this year to establish a new and almost unsurpassable record in which 109,000 square feet of space were necessary in order to supply the requirements of the exhibitors.

Your Board of Trustees is particularly pleased to have presented at this congress not only the usual technical sessions at which investigations and researches have been presented but feel that they have adjusted their program to the spirit of present-day activity, and by the incorporation of 14 technical sessions on national defense problems, conservation and substitution, presented for the membership a series of outstanding events of undoubted merit.

While 1941 has been one of the most successful years of the 23 years it has been my privilege to present reports, I should be neglectful of my duty to everyone if I did not take this opportunity to offer my profound indebtedness for the helpful co-operation I have received from the officers and trustees of the Society as well as a happy recognition of a close associationship and helpful co-operation from the members of the A.S.M. headquarters staff.

ELECTION OF OFFICERS

DR. O. E. HARDER, *Presiding*: Complying with the Constitution, I appointed on March 21, 1941, the following Nominating Committee, selected from the list of candidates suggested by eligible chapters prior to March 1, 1941.

John W. Harsch, Chairman (Philadelphia Chapter)
Arthur E. Focke (Indianapolis Chapter)
H. S. Jerabek (Northwest Chapter)
Henry J. Fischbeck (Hartford Chapter)
Carl R. Whittemore (Montreal Chapter)
W. R. Fraser (Springfield Chapter)
C. R. Wiggins (Rockford Chapter)

The Committee met in Philadelphia on May 19, 1941, and made the following nominations:

President—Bradley Stoughton, Lehigh University, Bethlehem, Pa. (1 year)

Vice-President—H. J. French, International Nickel Co., New York City (1 year)
Treasurer—Francis B. Foley, The Midvale Company, Philadelphia (2 years)
Trustee—Norman F. Tisdale, Molybdenum Corp. of America, Pittsburgh (2 years)
Trustee—Kent R. Van Horn, Aluminum Company of America, Cleveland (2 years)

A report of these nominations duly appeared in THE REVIEW for May, 1941.

I have been informed by the Secretary that no additional nominations were received prior to July 15, 1941, for any of the vacancies occurring on the Board of Trustees. Consequently the nominations were closed. I shall now call upon the Secretary to carry out the provisions of the Constitution in respect to the election of Officers.

W. H. EISENMAN: Conforming with the provisions and requirements of the Constitution of the Society, I hereby cast the unanimous vote of the members for the election of the aforenamed candidates, who were regularly nominated on May 19, 1941.

PRESIDENT HARDER: The provisions of the Constitution having been complied with, I hereby declare the candidates heretofore named to be duly and unanimously elected to the several specified offices, the terms of each beginning on the day following the close of this annual meeting.

. . . President Harder introduced the newly-elected trustees, and asked Professor Stoughton to say a word to the assembled members.

PROFESSOR STOUGHTON: When I think of the splendid and efficient men, and men of outstanding technical ability, who have held the office of President of this Society, it makes me very bashful to think that I am to have that place for one year. I thank the Society sincerely for electing me to this office.

PRESIDENT HARDER: Has anyone present anything to bring before the meeting for the benefit of the Society? If not, a motion to adjourn is in order. (Made, seconded, and unanimously carried.)

The meeting was then adjourned and President Harder introduced Dr. Edgar C. Bain, chairman of the Campbell Memorial Lecture, who in turn introduced Dr. Robert H. Mehl, Director, Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, who presented the Sixteenth Campbell Memorial Lecture entitled *The Structure and Rate of Formation of Pearlite,* which is published in this issue of TRANSACTIONS beginning on page 813.

THE ANNUAL BANQUET

On Thursday evening, October 23, 1941, the American Society for Metals was host to 1150 members and guests at its annual banquet held in the ballroom of the Benjamin Franklin Hotel, Philadelphia. Seated at the speakers' table were the following: John W. Harsch, chief engineer, Leeds & Northrup Co., and chairman Philadelphia Chapter of A.S.M.; Norman F. Tisdale, metallurgical engineer, Molybdenum Corporation of America and new trustee of the A.S.M.: Morris Asimow, metallurgist, Central Products Co., and joint recipient of the Henry Marion Howe Medal; Marcus A. Grossmann, director of research, Chicago District, Carnegie-Illinois Steel Corp. and joint recipient of the Henry Marion Howe Medal and trustee of the A.S.M.; William P. Woodside, vice-president, Climax Molybdenum Corp., founder-member and past-president, A.S.M.; Charles S. Redding, president, Leeds & Northrup Co.; Robert F. Mehl, director, Metals Research Laboratory and head of Department of Metallurgy, Carnegie Institute of Technology, and 1941 Campbell Memorial Lecturer; R. S. A. Dougherty, manager, Development and Research Department, Bethlehem Steel Co.; Francis B. Foley, superintendent of research, Midvale Co. and treasurer-elect of the A.S.M.; Lieutenant Colonel D. N. Hauseman, U.S.A., executive officer, Philadelphia Ordnance District; Kent R. Van Horn, research metallurgist, Aluminum Company of America, and treasurer of A.S.M. and trustee-elect for 1942; J. E. Lose, vice-president in charge of operations, Carnegie-Illinois Steel Corporation; Bradley Stoughton, professor of metallurgy, Lehigh University, and vice-president and president-elect of A.S.M.; William L. Shirer, Columbia Broadcasting System's Foreign Correspondent and News Commentator; Oscar E. Harder, assistant director, Battelle Memorial Institute and president of A.S.M.; C. F. Hood, president American Steel & Wire Company; James P. Gill, chief metallurgist, Vanadium Alloys Steel Co. and past-president of A.S.M.; J. V. Honeycutt, assistant vice-president in charge of sales, Bethlehem Steel Co.; Herbert J. French, in charge of alloy steel and iron development, International Nickel Co., Inc., and trustee and vice-president-elect of A.S.M.; Brigadier General Walter P. Boatwright, U.S.A., executive officer, Frankford Arsenal; J. M. Ellis, general sales manager, Bethlehem Steel Co.; Albert L. Marsh, president, Hoskins Manufacturing Co., and recipient of the Albert Sauveur Achievement Award for 1941;

Rear Admiral A. E. Watson, U.S.N., commandant, United States Navy Yard; Robert L. Johnson, president, Temple University; R. E. Zimmerman, vice-president in charge of research, United States Steel Corp.; Charles Y. Clayton, professor of metallurgical engineering, Missouri School of Mines and Metallurgy, and trustee of A.S.M.; Edward L. Bartholomew, chief engineer, United Shoe Machinery Corp., and trustee of A.S.M.; Franklin H. Pennell, metallurgist, DeLaval Steam Turbine Co. and secretary of Philadelphia Chapter of A.S.M.; W. H. Eisenman, secretary of the American Society for Metals.

Dr. Oscar E. Harder opened the dinner meeting by expressing the best wishes of the officers and trustees to the assembled members and guests and then introduced to the audience those seated at the speakers table.

Presentation of the Past-President's Medal was made to James P. Gill, who retired from the Board of Trustees at the close of this meeting.

Following this, presentation of a certificate of appreciation was made to Dr. Robert F. Mehl who gave the Edward De Mille Campbell Memorial Lecture at this convention.

Presentation of the Henry Marion Howe Medal

The first Henry Marion Howe Medal was awarded by this Society in 1922. This medal is award for the paper of highest merit published by the Society during the preceding year. This year the papers considered were those published in the September and December 1939 TRANSACTIONS, the March, June, September 1940 TRANSACTIONS, the 1938 Symposium on "Hardenability of Alloy Steels" and the 1939 Symposium "Age Hardening of Metals". The five preliminary committees selected ten papers which were referred to the Final Committee, which in turn selected the paper of highest merit. Upon the recommendation of the Final Committee and with the approval of the Board of Trustees, the award this year is for the paper "Hardenability, its Relation to Quenching, and Some Quantitative Data" published in the 1938 Symposium "Hardenability of Alloy Steels" by Dr. M. A. Grossmann, Dr. M. Asimow, and Dr. S. F. Urban. It gives me great pleasure to present, on behalf of the American Society for Metals, the Henry Marion Howe Medal and Certificate for 1941 to:

Dr. M. A. Grossmann, Director of Research, Carnegie-Illinois Steel Corp., Chicago,
Dr. M. Asimow, Manager, Central Metals Products Co., Los Angeles, Calif., and
Dr. S. F. Urban, Metallurgist, South Works, Carnegie-Illinois Steel Corp., Chicago.

Presentation of Sauveur Achievement Award to Albert L. Marsch

The Sauveur Achievement Award was established by the American Society for Metals in 1934, to be given in recognition of outstanding contributions to developments in the field of metallurgy, and very fittingly the first award was to the late Professor Sauveur, in whose honor it had been named. The candidate for this Award is selected by the Past Presidents of the Society. This year Albert L. Marsch, President and General Manager of the Hoskins Manufacturing Company of Detroit, has been selected to receive this honor. I am taking this opportunity to tell you briefly of some of the outstanding accomplishments which have been the basis for this Award.

Mr. Marsch was born at Pontiac, Illinois, and following his graduation from the public schools he attended the University of Illinois, from which he received the degree of Bachelor of Science in Chemical Engineering. One of his early jobs after leaving the University of Illinois was with the Chicago Storage Battery Company and there he became interested in thermocouples and started research work to make an improved thermocouple. This research led to a patent, "Thermo-Electric Element", which was issued in 1905. This was a development which led to the now well-known Chromel-Alumel thermocouple. In making electrical measurements on chromel he discovered its high electrical resistance. This property, combined with its high melting point and strong resistance to oxidation, pointed to its value as an electrical resistance element, a development for which he received a patent in 1906. This Marsch patent, relating to electrical resistance elements, was contested in the courts and after long litigation was decided in his favor in 1914.

Mr. Marsch was instrumental in organizing The Hoskins Manufacturing Company in 1908, of which he was named Chief Engineer and made a Director. He soon became Superintendent and has been General Manager since 1914, and has been President and General Manager since 1932.

In 1936, the John Price Wetherill Medal was awarded to Mr. Marsch by the Franklin Institute, "for discoveries or inventions in the physical sciences, or for new and important combinations of principles or methods already known".

He is a Director of the Peerless Cement Company. He has been a valuable influence in the progress and development in his chosen field of specialization and he is well known for his willingness and ability to help others in the solution of problems.

Mr. Marsch, upon the unanimous selection of the Past Presidents of the American Society for Metals and with the approval of the Board of Trustees, it gives me great pleasure, on behalf of the American Society for Metals, to present you with the Albert Sauveur Achievement Award Plaque and Scroll.

Reply by Albert L. Marsch

MR. MARSCH: Dr. Harder, members of the American Society for Metals, and guests:

Nickel-chromium alloys have come into wide use in thermocouples for the measurements of high temperatures and in heating elements for electric furnaces and domestic appliances. Perhaps you may be interested in hearing about the discovery of properties which led to these applications.

My first experiments on nickel-chromium alloys were made in 1903. Previous reading on the subject of thermocouples led me to think that a better positive element could be found. In a Chicago shop where I was working there was a blacksmith's forge that was seldom used. This suggested a possible means of melting some nickel-chromium alloys that I had in mind to try and as soon as there was some spare time the attempt was made. After a number of trials with a thick bed of coal on the forge, and by the use of small battersea assay crucibles to hold the charge, melting was successfully done. The temperature required was just about the limit for the crucibles and often they would become so soft that they could not be removed from the fire for casting the metal into small bars.

By this method a series of samples was produced having chromium contents up to about 20 per cent. Thin pieces were needed for testing and had to be cut from the bars with a hacksaw. The bars were not ductile but were strong enough for the purpose. Milli-

volt tests on the thin strips were made using a piece of copper wire for the other element of the couple. The tests showed a positive value of good magnitude which was the desired result.

The composition that gave the best value was 90 per cent nickel and 10 per cent chromium. Incidentally, the standard element today contains 9.5 per cent chromium.

Other tests showed a remarkable resistance to destructive oxidation at high temperatures.

A few months later I had access to a wheatstone bridge and found the electrical resistance was high and especially so in the 20 per cent chromium alloy. The alloys as made with the impure powdered chromium then available showed the desirable properties for thermocouple and electric heating elements except for the lack of ductility.

About that time a good grade of chromium, made by the aluminum reduction process, came onto the market. With it ductile alloys were made in a small electric furnace and the commercial use became possible. The blacksmith's forge was abandoned, but it had served its purpose.

The Albert Sauveur Award presented to me by your Society is sincerely appreciated and I wish to thank the Past Presidents, Officers and Directors for their favorable consideration.

At the conclusion of these presentations of awards Dr. Harder then introduced the speaker of the evening, the world famous correspondent and commentator William L. Shirer, who gave a very interesting address on the European situation.

Statement of the ownership, management, circulation, etc., required by the acts of Congress of August 24, 1912, and March 3, 1933, of TRANSACTIONS of American Society for Metals, published quarterly at Cleveland, Ohio, for October 1, 1941, State of Ohio, county of Cuyahoga, ss. Before me, a notary public, in and for the State and county aforesaid, personally appeared Ray T. Bayless, who, having been duly sworn according to law, deposes and says that he is the editor of the TRANSACTIONS of the American Society for Metals, and that the following is, to the best of his knowledge and belief, a true statement of the ownership, management, etc., of the aforesaid publication for the date shown in the above caption, required by the Act of August 24, 1912, as amended by the Act of March 3, 1933, embodied in section 537, Postal Laws and Regulations, to wit:

1.—That the names and addresses of the publisher, editor, managing editor, and business managers are: Publisher, American Society for Metals, 7301 Euclid Ave., Cleveland, O.; Editor and Managing Editor, Ray T. Bayless, 7301 Euclid Ave., Cleveland, O.; Business Manager, W. H. Eisenman, 7301 Euclid Ave., Cleveland, O.

2.—That the owner is: The American Society for Metals, 7301 Euclid Ave., Cleveland, Ohio, which is an educational institution, the officers being: President, O. E. Harder; Vice-President, Bradley Stoughton; Secretary, W. H. Eisenman; Treasurer, K. R. Van Horn; Trustees: J. P. Gill, H. J. French, M. A. Grossmann, E. L. Bartholomew, C. Y. Clayton. All officers as above, 7301 Euclid Ave., Cleveland, Ohio.

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(Seal) Arthur T. Wehrle, notary public.

(My commission expires January 20, 1944)

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